

SOUTHERN CALIFORNIA PARTICLE SUPERSITE

Progress Report for Period November 1, 2000 – February 1, 2001

United States Environmental Protection Agency

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1. Introduction

The research activities of our Southern California Supersite (SCS) are integral part of the overall themes of the Southern California Center for Ambient Particulate Matter (SCCAPM), a 5-year program that we were awarded through EPA's STAR initiative approximately one year ago

The overall objective of the Southern California Particle Supersite is to conduct research and monitoring that contributes to a better understanding of the measurement, sources, size distribution, chemical composition and physical state, spatial and temporal variability, and health effects of suspended particulate matter (PM) in the Los Angeles Basin (LAB). The specific research objectives are:

1. To characterize PM, its constituents and precursors, to better understand sources and transport which may affect human exposure and to support development of State Implementation Plans (SIPs).
2. To obtain atmospheric measurements for the support of health studies that are designed to address causal factors, etiologic pathways and mechanisms of PM related morbidity and mortality with particular emphasis on PM source-receptor-exposure-effects pathways.
3. To conduct methods testing that will enable comparisons and evaluation of different technologies for characterizing PM, including evaluation of new instrumentation, sampling methods and federal reference methods.

This report addresses the period from November 1, 2000 through February 1, 2001

2. Particulate sampling at First SCS Site (Rancho Los Amigos National Rehabilitation Medical Center)

We have continued our PM sampling at Rancho Los Amigos (south-central Los Angeles), in conjunction with ongoing human inhalation exposure studies to concentrated PM, as well as studies in which we use our coarse, fine and ultrafine concentrators to collect size-fractionated PM for *in vitro* characterization of PM toxicity. These studies are part of our PM Center Toxicology core investigations. The studies involving human exposures to concentrated PM is directed by Dr. Henry Gong (USC Keck School of Medicine). Our *in vitro* studies are being carried out by Dr. A. Nel (UCLA School of Medicine). In addition to Dr. Nel and his group, we have collaborative arrangements with Dr. Robert Devlin, of the U.S. EPA Human Studies laboratory (Chapel Hill, North Carolina) to conduct toxicity studies in a human epithelial cell line. Dr. Devlin will determine changes in cytokine levels and eicosinoid levels in these cells after exposure to particle samples collected from the same freeway sites. Our continuous and time-integrated data serve all of the aforementioned studies.

2a. Continuous Size Distributions

Near-continuous (i.e., 15-min averaged) size distributions for 0.01 – 20 μm particles were generated by means of the SMPS (0.01- 0.8 μm) and APS (0.5 – 20 μm) monitors. The size distributions generated by the two instruments were matched at 0.5 μm using a standard particle with a density of 1.6 g/ml. Figures A1-A9 (see Appendix) present typical size distribution patterns consisting of four time intervals for each day (6 am – 10 am; 10 am – 3 pm; 3 pm – 8 pm; 8 pm – 6 am). These time periods were selected to capture morning, mid-day, evening, and nighttime traffic patterns. The highest PM concentrations in most of the size distributions were observed in the 6 am – 10 am period, followed by the 8 pm – 6 am period. The high PM concentrations in the 6am – 10 am period are obviously due to the contributions of morning

traffic. The high PM concentrations at night are due to the 24-hour heavy diesel truck traffic in the nearby 710 (Long Beach) Freeway, combined with the low mixing layer of the atmosphere at that time. The Rancho' Supersite monitoring site is located approximately 1.6 km east of freeway 710, thus directly downwind of the freeway, as we've observed the prevailing winds to from the South West, on the average.

The size distributions obtained in October 2000 indicate that the accumulation mode of ambient PM is distinctly bimodal at least during the 6 am – 10 am period, with two separate peaks at approximately 0.2 – 0.3 and 0.6-0.7 μm . The first mode (condensation mode) consists of mainly combustion-generated particles that have agglomerated from their original ultrafine to a somewhat larger size and by products of gas-to-particle conversion mechanisms, which are more pronounced during the photochemical period in Los Angeles (ranging from June to November). The bimodality of the distributions becomes less pronounced (and in some cases disappears) as the day progresses, due to the decrease in relative humidity, which would impair growth of the hygroscopic components of PM. There is no substantial difference between weekday (October 4, 10) and weekend (October 7 and 21) days. Of particular interest are the data plotted in Figure A2 (October 10, 2000). During this day, the wind speed was on the average 8-10 mph, which is substantially higher than the typically quasi-stagnant conditions in south central Los Angeles (mostly varying from 1 to 3 mph). These wind conditions may explain the low fine PM concentrations, with the exception of the peaks in the ultrafine mode, which were observed during the morning and evening traffic periods. These meteorological conditions would also favor higher coarse PM concentrations, shifting the size distribution curve towards the larger sizes of the coarse mode (i.e., 5-6 μm). This shift is also indicated by the data plotted in Figure A2.

By contrast, stagnation conditions prevailed in south-central Los Angeles during the week of October 17 – 21, 2000, with the average wind speed during the sampling periods being less than 1 mph. Two-hour averaged fine PM concentrations measured by either the MOUDI or Partisol during these two days ranged from 80 to 146 $\mu\text{g}/\text{m}^3$. These conditions are expected to

result in high fine PM concentrations in locations such as Downey, which is primarily impacted by vehicular emissions from nearby freeways, while the relatively low coarse PM concentrations may be explained by the lack of sufficient wind velocity to either generate or transport coarse particles.

The size distributions obtaining during the somewhat cooler months of December and January indicate that the accumulation mode displays a single peak in the droplet mode, between 0.6-0.8 μm . During this period, particle formation due to photochemistry is less pronounced. The relatively higher RH conditions compared to the previous period cause particles to grow to 0.5-0.7 μm .

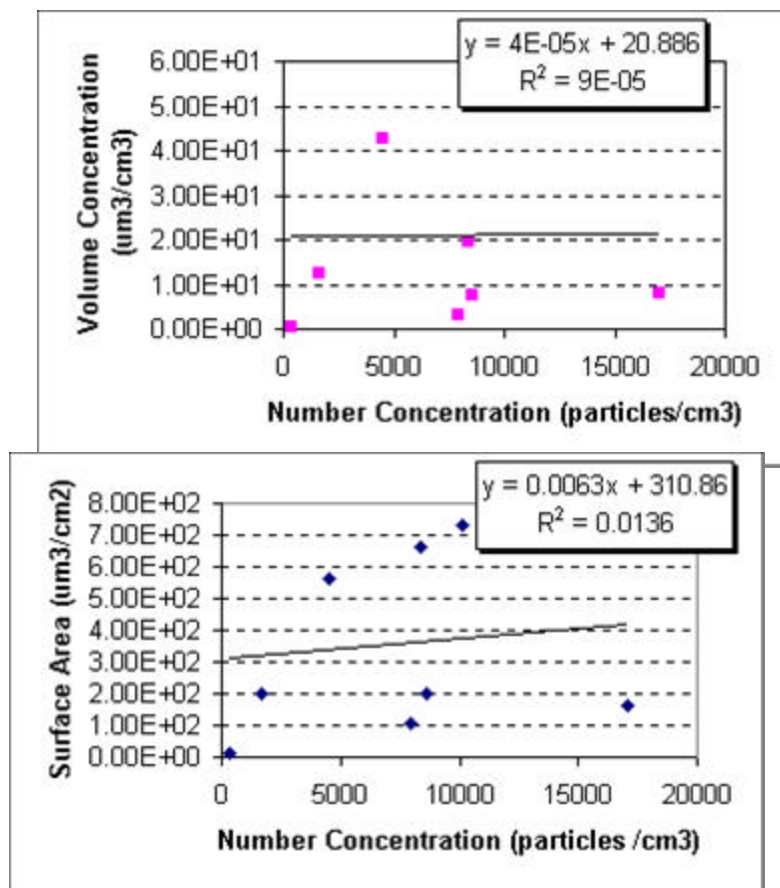
Figures A10-A18 show selected time series plots of total hourly concentrations of 0.01 – 0.8 μm particles based on number, surface area and volume, obtained by means of the SMPS. It should be noted that the number and surface area concentrations associated with the 0.01- 0.8 μm range account for nearly the entire PM_{2.5} fraction, respectively, whereas the fraction, by mass, associated with that size range was typically 75 to 85% of the total PM_{2.5}. The graphs indicate two distinct peaks Number Concentrations, occurring roughly between 5- 7 am and 5-7 pm (i.e., during the morning and evening traffic peak hours).

Table 1 gives a summary of the obtained correlation coefficients for selected sampling days. For most of the days, the hourly number, surface, and volume based concentrations are highly correlated (R^2 varying from 0.80-0.99). Even at days in which these correlations seem to be weaker, such as October 7, 2000 or January 18, 2001, the coefficients of determination (R^2) between the number, surface and volume distributions during the traffic hours (i.e., 6 am – 10 am and 3 pm – 8 pm) increase from the range of 0.15-0.3 to higher than 0.80.

Table 1. Correlation Between the Hourly Number, Surface and Volume Concentrations of Fine PM in Downey.

Date	Number-Surface Corr. Coeff. (over 24 hr)	Number-Volume Corr. Coeff. (Over 24 hr)	Number-Volume Corr. Coeff. (From 6 am – 10 am)	Number-Volume Corr. Coeff. (From 3 pm –8 pm)
10/7/00	0.40	0.14	0.99	0.98
10/10/00	0.87	0.63	0.95	0.93
10/21/00	0.95	0.95		
12/10/00	0.94	0.93		
12/28/00	0.92	0.87		
12/29/00	0.78	0.94		
1/3/01	0.81	0.14	0.94	0.90
1/18/01	0.39	0.14	0.99	0.99
1/21/01	0.95	0.96		

The obtained high correlations are in complete disagreement with data obtained during the Atlanta Supersite measurement program, in which no apparent correlations were found between the number, surface area and volume concentrations of PM_{2.5} (Woo et al., *Aerosol Sci and Technol.*, 34, pp 57-65, 2001). Interestingly, when the 24-hour averaged surface area and volume concentrations are plotted against the 24-hour average number concentrations, very weak correlations are obtained, as indicated by the data plotted in the following figures..



During the following few months, we will conduct the following analysis of our continuous data:

- a. We will continue the investigation of the relationship between 1-hr and 24-hr averaged particle number, surface and volume concentrations. These investigations will be conducted for days with varying meteorological conditions, including high and low wind speed and relative humidity. Separate correlations will be conducted for each of the morning and evening traffic, mid-day and night-time periods in order to improve our understanding of the relationship between ultrafine PM emitted from mobile sources and the mass concentrations measured down wind of these sources.

- b. We will investigate the occurrence and prevalence of the various sub-modes of PM_{2.5} as a function of RH, temperature and wind speed in our next Supersite location in Riverside.
- c. We will investigate the relationship between the average size of coarse mode particles, expressed by means of the mass median diameter (MMD), and wind speed. As part of this investigation, we will also examine the relationship between the fine-to-coarse PM concentration ratio vs wind speed. We will investigate the hypothesis that both coarse PM MMD and mass concentrations decrease as the wind speed decreases. Part of this investigation has been initiated during the characterization of our continuous coarse PM monitor. Preliminary (and encouraging) results are described in section 7 c.

2b. Measurement of the Spatial and Seasonal Variation of Ultrafine PM in the LAB and their Relation to Sources

The purpose of this research is to determine whether ultrafine particle concentrations are affected mainly by local sources rather than having a uniform spatial distribution. Starting in October of 2000, the Air Resources Board of California placed 12 Condensation Particle Counters (TSI CPC, 3022) in each of the USC Children's Health Study (CHS) sites. These sites include Long Beach, Fontana, Lake Elsinore, Lancaster, Upland, Rubidoux, Mira Loma, Glendora and the University of California Riverside campus.

As part of our data analysis, the 5-min, 1-hr and 24-hour averaged ultrafine number concentrations measured in each site will be correlated. In addition, in every site, the degree of correlation between the 1-hour averaged particle number concentrations, carbon monoxide (CO) and nitrogen dioxide (NO₂) will be investigated. This data analysis has already started and indicative results are shown in Figure A19. The data represent particle number, NO_x and CO concentrations obtained during the second half of December in Lancaster, CA, a "desert" site. The monitoring site is located about 5 km from the nearest freeway or busy street. In comparison, the data plotted in Figure A20 display the typical bimodal diurnal pattern of particle

number concentrations that we observed in our urban site at Rancho Los Amigos, peaking during the morning and evening traffic hours. The bimodal nature of these number-based particle distributions is somewhat less pronounced during Sunday December 17, 2000. Of particular note is the very high degree of correlation between particle number, nitrogen dioxide and carbon monoxide concentrations during this period (R^2 of 0.97 and 0.93, respectively), which is somewhat surprising considering that the site is located more than 5 km away from vehicular sources to be affected by traffic patterns and density. Finally, there seems to be a reasonable correlation between PM number and PM_{2.5} mass-based concentrations measured by the TEOM ($R^2 = 0.68$). This degree of correlation is also surprising, considering that the aerosol is heated to 50 degrees C in the TEOM prior to collection by the oscillating filter, where inevitable losses of semivolatile PM constituents are expected to occur. More data will be obtained from the 12 CHS sites to investigate whether this degree of correlation will persist and how it will depend on the site distance to a nearby freeway or busy street. Finally, we will investigate the relationship between the hourly concentrations of ultrafine counts and the hourly concentrations of EC and PAH measured by the Aethalometer.

3. Time-integrated data

Our current sampling scheme involves the use of a MOUDI for 24-hour averages, size-fractionated measurements of ambient and concentrated PM mass and chemical composition. Sampling is conducted approximately once every 6th day.

In each run, consistent with our original Supersite proposal, we have used three collocated Micro-Orifice Uniform Deposit Impactors (MOUDI) to group PM into the following size ranges:

- $<0.1 \mu\text{m}$ (ultrafine particles)
- $0.1\text{-}0.35 \mu\text{m}$ (accumulation mode, “condensation” sub-mode)
- $0.35\text{-}1.0 \mu\text{m}$ (accumulation mode, “droplet” sub-mode)

- 1.0-2.5 μm (“intermediate” mode)
- 2.5-10 μm (coarse particles)

In addition to mass concentration, the following chemical components have been analyzed within these size groups:

- inorganic ions (i.e., sulfate, nitrate, ammonium)
- trace elements and metals
- elemental and organic carbon (EC/OC) content
- concentrations of polycyclic aromatic hydrocarbons (PAH)

Ambient data are averaged over 24 hours, whereas data corresponding to concentrated PM are only averaged over two hours, as this is the typical duration of the human exposure experiments, conducted simultaneously with PM sampling.

In addition to the MOUDI, we employ two dichotomous samplers:

- Partisol-Plus sampler (Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co. Inc., Albany, NY; and
- USC Dichotomous Sampler, operating at 50 LPM, which will be described in greater detail in section 7a (Development of a Continuous Coarse PM Monitor)

These two samplers are used to provide data on mass and chemical compositions of coarse (2.5 –10 μm) and fine (0-2.5 μm) particles in the following time intervals: 6 am –10 am; 10 am – 3 pm; 3 pm- 8 pm; 8 pm – 6 am. These experiments are also conducted approximately once every 6th days and concurrently to the MOUDI sampling days. In each of the coarse and fine particle channels of the Partisol sampler we place quartz filters for PM collections, whereas Teflon filters are placed in the coarse and fine PM channels of the USC Dichotomous sampler. At the end of each test, a 0.2 cm^2 portion of the Partisol quartz filters are removed and sent for elemental and organic carbon (EC/OC) analysis, whereas the remaining filter was extracted with milli-Q water to determine the inorganic ion content of coarse and fine PM. The USC

Dichotomous Sampler filters were first weighed to determine the mass concentrations and then analyzed by means of XRF to determine the trace element and metal content of coarse and fine PM. Sampling has been completed for a total of 12 weeks covering the period from October 3, 2000 to January 21, 2001 and the fine and coarse mode samples have been sent for chemical analysis. At present, we do not have data from the chemical analysis of this time series, but we expect to have them available in our next progress report. The only data that we have available are size-fractionated, 24-hour averaged concentrations for trace elements and metals, based on nine 24-hour experiments conducted in the period between October 3 and December 29, 2000. These data have been obtained by means of the MOUDI samplers. Figure A21 shows a plot of the average partition by mass in the five PM size modes of the 15 most predominant metals and elements at Rancho Los Amigos. The data plotted in Figure A 21 reveal that Al, Si, Fe, Ca, K, Ti and Ba are almost exclusively partitioned in the super micrometer size range, with more than 50% by mass found in the coarse mode. For Si, Fe, Ca, Ti, Ba, Zn and Cu, roughly one-third of the metal mass is associated with the intermediate mode. Combustion-generated metals and elements, such as Zn, Cu, Mn, Pb, Cr, Sn, V and Ni are associated largely with PM_{2.5}, with mass fractions varying from 0.75 to 0.93. There is a notable increase in the ultrafine fraction for these metals, with the highest fraction observed for Ni (about 20% by mass). Ultrafine and condensation mode particles account for more than 40% of Pb, Cr, Sn, V and Ni.

4. Characterization of PAH Derivatives in PM_{2.5} at a Source Site Impacted by Vehicle Emissions

Introduction

The goal of our sampling at Downey, CA was to characterize the PAH and PAH-derivatives present at this source site and to investigate the atmospheric chemistry occurring. Three types of samples were taken to span the range of volatility of the PAH and derivatives:

Tenax samples for gas-phase PAH, polyurethane foam (PUF) samples for semi-volatile PAH and nitro-PAH, and Hi-vol filter samples for particle-associated species. To characterize the Downey site, eight 12-hr daytime and eight 12-hr nighttime samples have been collected. To date the gas-phase PAH on the Tenax samples have been analyzed, as well as one particle sample to investigate the nitropyrenes and nitrofluoranthenes present. The results of these gas-phase PAH data will be used to composite samples prior to analysis of the less volatile and lower abundance PAH and derivatives.

Results

Gas-Phase PAH. The gas-phase PAH that were analyzed by gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring (SIM) were: naphthalene, 1- and 2-methylnaphthalene, acenaphthylene, biphenyl, acenaphthene and fluorene. In addition, the molecular ion for the C₂-naphthalenes was included to investigate the abundance of these alkyl-PAH. Naphthalene, 1- and 2-methylnaphthalene and biphenyl were monitored so that when their nitro-derivatives (sampled on the PUF plugs) are analyzed, the amount of nitro-PAH formed by atmospheric chemistry can be determined. All four of these precursor PAH were measured in each of the replicate 12-hr samples. Acenaphthylene was also observed in all samples, while acenaphthene and fluorene were only observed occasionally, mainly in nighttime samples. The C₂-naphthalenes were also present in all samples and it was anticipated, therefore, that by comparing the daytime versus nighttime naphthalene and alkyl-naphthalene concentrations it will be possible to estimate the extent of hydroxyl radical (OH) reaction occurring at Downey. Presently the rate constant for reaction of 2,3-dimethylnaphthalene is the only C₂-naphthalene rate constant available (see table below), but we anticipate measuring those for the remaining eleven C₂-naphthalenes (funding for these kinetic studies is presently being sought).

In this progress report, the gas-phase PAH data for the eight day/night sample pairs are reported and an example of how the hydroxyl radical chemistry can be examined using such data is given. The Downey, CA site is heavily impacted by vehicle emissions and was chosen

as a sampling site to characterize the PAH and nitro-PAH ratios and profiles resulting mainly from direct vehicle emissions, and in these winter samples (November-January) the daytime hydroxyl radical reaction of the gas-phase PAH is expected to be rather limited because of shorter daytime hours.

Table 1. Room Temperature Rate Constants for Reaction with the OH Radical and Resulting Atmospheric Lifetimes (τ).

PAH	$10^{11} \times k_{OH}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	t^a
Naphthalene	2.30	6.4 hours
1-Methylnaphthalene	5.30	2.8 hours
2-Methylnaphthalene	5.23	2.8 hours
2,3-Dimethylnaphthalene	7.68	1.9 hours
Acenaphthylene ^b	10.9	1.3 hours
Biphenyl	0.71	21 hours

^aAssuming an OH radical concentration of $1.9 \times 10^6 \text{ molecule cm}^{-3}$.

^bWill also react with O_3 .

If the volatile PAH have vehicle emissions as their dominant source, the nighttime ratios of the PAH should be characteristic of the vehicle emissions and should be constant if no nighttime chemistry is occurring. For the eight nighttime samples, ratios of the individual PAH to naphthalene were quite constant (ratio \pm one standard deviation) consistent with Downey being heavily vehicle impacted:

$$\begin{aligned}
 &1\text{-Methylnaphthalene/Naphthalene} = 0.19 \pm 0.02 \\
 &2\text{-Methylnaphthalene/Naphthalene} = 0.40 \pm 0.05 \\
 &\text{Biphenyl/Naphthalene} = 0.040 \pm 0.008 \\
 &\text{Acenaphthylene/Naphthalene} = 0.036 \pm 0.014
 \end{aligned}$$

Replicate Tenax samples were collected and the precision calculated as the standard deviations of the relative difference of the measured mixing ratios of 15 duplicate samples was: naphthalene \pm 2%, 1-methylnaphthalene \pm 8%, 2-methylnaphthalene \pm 7%, biphenyl \pm 5% and

acenaphthylene \pm 18%. As may be seen from the data tables below, with the exception of the December 7-8 samples, the nighttime concentrations were greater than the daytime concentrations, probably reflecting a lower nighttime mixing layer. The constant night/day ratio for all the volatile PAH for the December 7-8 sample (0.3) clearly shows the dominant effect of meteorology on this day/night sample pair.

Naphthalene (ng/m³)

Date	Day	Night	Night/Day
November 2-3, 2000	486	1018*	2.1
November 9-10, 2000	226	464	2.1
November 16-17, 2000	441	777	1.8
Nov. 30 - Dec. 1, 2000	527	1121	2.1
December 7-8, 2000	662	202	0.3
December 14-15, 2000	449	987	2.2
December 19-20, 2000	492	1589	3.2
January 4-5, 2001	632	1506	2.4

1-Methylnaphthalene (ng/m³)

Date	Day	Night	Night/Day
November 2-3, 2000	87	195*	2.2
November 9-10, 2000	38	86	2.3
November 16-17, 2000	82	163	2.0
Nov. 30 - Dec. 1, 2000	89	198	2.2
December 7-8, 2000	142	46	0.3
December 14-15, 2000	93	178	1.9
December 19-20, 2000	103	269	2.6
January 4-5, 2001	110	236	2.1

2-Methylnaphthalene (ng/m³)

Date	Day	Night	Night/Day
November 2-3, 2000	184	416*	2.3
November 9-10, 2000	85	183	2.2
November 16-17, 2000	179	342	1.9
Nov. 30 - Dec. 1, 2000	204	446	2.2
December 7-8, 2000	308	100	0.3
December 14-15, 2000	195	374	1.9
December 19-20, 2000	216	580	2.7
January 4-5, 2001	228	498	2.2

Biphenyl (ng/m³)

Date	Day	Night	Night/Day
November 2-3, 2000	21	37*	1.8
November 9-10, 2000	8.0	17	2.1
November 16-17, 2000	16	41	2.6
Nov. 30 - Dec. 1, 2000	20	43	2.2
December 7-8, 2000	26	8.7	0.3
December 14-15, 2000	15	40	2.7
December 19-20, 2000	24	42	1.8
January 4-5, 2001	22	66	3.0

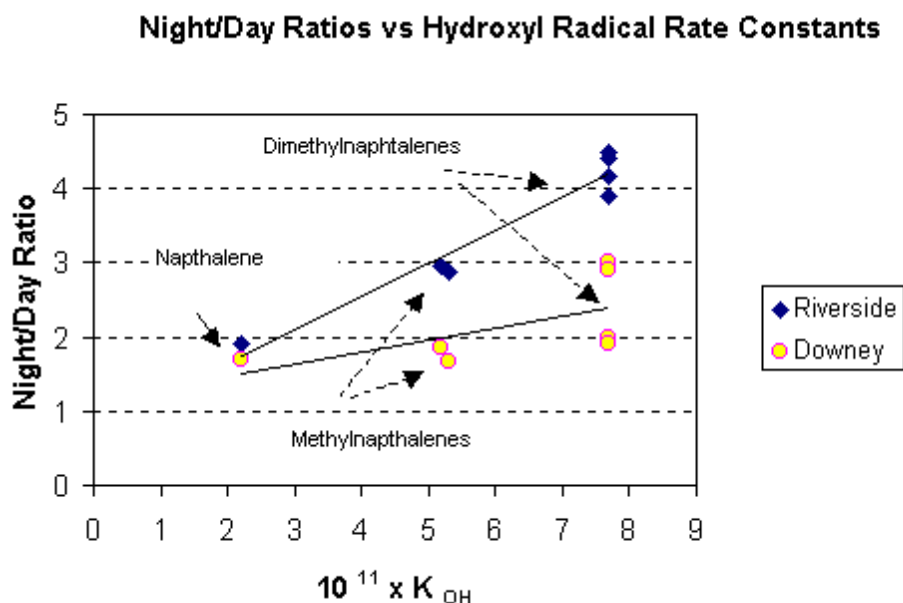
Acenaphthylene (ng/m³)

Date	Day	Night	Night/Day
November 2-3, 2000	6.7	34*	5.1
November 9-10, 2000	0.8	19	24
November 16-17, 2000	8.0	38	4.8
Nov. 30 - Dec. 1, 2000	7.3	46	6.3
December 7-8, 2000	7.2	1.9	0.3
December 14-15, 2000	6.4	52	8.1
December 19-20, 2000	11	51	4.6
January 4-5, 2001	8.3	42	5.1

*Single Tenax sample.

Acenaphthylene has the highest rate constant (see Table 1) for reaction with the OH radical and also had a consistently higher night/day ratio. Unfortunately, acenaphthylene also reacts with O₃ and caution must be exercised in attributing its higher nighttime value to daytime OH radical chemistry. As seen in Table 1, the single C₂-naphthalene for which a rate constant has been measured is over 3 times as reactive as naphthalene. Therefore, although the C₂-naphthalenes were not quantified (standards have only recently been purchased), the ratio of their night/day chromatographic peak areas can be obtained from the data for their molecular ion and used to investigate the occurrence of OH radical chemistry. The November 16-17 sample shown on the figure below is typical of the Downey samples in that little difference was seen between the night/day ratios of naphthalene and the methylnaphthalenes, indicating little

OH radical reaction. Also plotted on the figure is data taken in Riverside in August during the Southern California Ozone Study (SCOS97). In the Riverside sample, the night/day ratio clearly increases with alkyl-substitution of naphthalene. All the dimethylnaphthalenes are shown plotted against the rate constant for 2,3-dimethylnaphthalene and thus the line will be better delineated when the rate constants have been measured for each dimethylnaphthalene. Not shown on the figure are 1- and 2-ethylnaphthalene, which were observed in all the samples. Based on the ambient data, the rate constant for the ethylnaphthalenes is more similar to those of the methylnaphthalenes than to 2,3-dimethylnaphthalene, which is consistent with the relative reactivities of ethylbenzene, toluene, and the xylenes toward reaction with the OH radical.



Preliminary Analysis of Nitrofluoranthenes and Nitropyrenes. A single Hi-vol filter from the nighttime Nov. 19-20, 2000 sample collection was spiked with 50 ng of 1-nitropyrene- d_9 , Soxhlet extracted overnight in dichloromethane, fractionated by normal phase high-performance liquid chromatography (HPLC) using a silica column and analyzed by GC/MS with SIM. 2-

Nitrofluoranthene, 1-nitropyrene and 2-nitropyrene were identified in this sample. Based on the ratio of the molecular ion of the 1-nitropyrene- d_9 and the molecular ion of 1-nitropyrene and on the approximately 500 m³ sample size, the 1-nitropyrene concentration is estimated at ~1 pg/m³. The 2-nitrofluoranthene concentration exceeded that of the 1-nitropyrene, suggesting that the vehicle traffic at the Downey site is not a strong source of 1-nitropyrene. If the source of the 1-nitropyrene is direct emission in vehicle exhaust and the source of the 2-nitrofluoranthene is atmospheric reaction of gas-phase fluoranthene, this may result in different relative abundances of these two nitro-PAH isomers in different particle size fractions. The 1-nitropyrene would be expected to be on small particles, originating from for example diesel emissions, while the 2-nitrofluoranthene would be expected to be distributed more on the basis of particle surface area since the 2-nitrofluoranthene is formed in the gas-phase and then condenses onto available ambient particles.

Future Plans

Based on the limited OH radical chemistry evidenced by the gas-phase PAH data obtained at Downey, only two composite samples will be used for additional analysis at this time: a daytime composite and a nighttime composite. As with the Tenax samples, replicate twelve-hour PUF/Hi-vol samples were collected and the samples not used for analysis at this time will be archived for future analysis and anticipated comparison of polar PAH-derivatives at this source site with sites where significant atmospheric chemistry has modified the PAH emissions. Single PUF samples from November 2, November 30 and January 4 will be composited for extraction, HPLC separation and GC/MS analysis of phenanthrene, methylphenanthrenes (abundant in diesel exhaust), fluoranthene and pyrene in a non-polar HPLC fraction and nitronaphthalenes, methylnitronaphthalenes and 3-nitrobiphenyl in a more polar HPLC fraction. A second PUF composite sample from the nights of Nov. 2-3, Nov. 30-Dec. 1 and Jan. 4-5 will also be analyzed for the semi-volatile PAH and the 2- and 3-ring nitro-PAH.

Additionally the corresponding filter particle samples (note that particle size selection was not done during the sampling) will constitute a daytime composite sample and a nighttime composite sample that will be analyzed for the presence of nitrofluoranthenes and nitropyrenes by GC/MS analysis following HPLC fractionation. After the composite samples have been analyzed for nitrofluoranthenes and nitropyrenes, it should be possible to estimate the air volume of size-fractionated particles that would be required to investigate possible differences in the 1-nitropyrene versus 2-nitrofluoranthene particle size distributions.

Sampling and analysis procedures at the next sampling site, which is anticipated to be Riverside, will be similar to those described here. As noted above, standards of the 12 C₂-naphthalenes have been purchased and at the next sampling site, the C₂-naphthalenes collected on the Tenax samples will be quantified in addition to the other gas-phase PAH monitored at Downey.

5. Size Distribution and Spatial Seasonal Variation of PAHs in the LAB

One of the activities of our Supersite project involves measurements of the seasonal and spatial variation of size-segregated PAHs in the Los Angeles basin air. The location of the SCPCS sampling sites, near sources and downwind from major sources, provide an opportunity to determine whether PAH partitioning occurs during transport across the Los Angeles Basin. If partitioning occurs during atmospheric transport, it might alter the size distribution of certain PAH which may lead to changes in their transport and deposition in the human respiratory system.

During collection on filters, semivolatile organic compounds (SVOC) such as low molecular weight PAHs can both adsorb on and desorb from particles during sampling, leading to positive and negative sampling artifacts, respectively. The use of a denuder ahead of a filter has been proposed as a means of reducing such sampling artifacts. However, removal of

SVOC may alter the gas/particle thermodynamic equilibrium and potentially lead to distortions in the size distribution of the sample collected.

In order to evaluate if such artifacts occur during *size-resolved* sampling of particulate PAHs, we designed a series of field experiments where samples were collected using two co-located MOUDI impactors: One with a gas trapping system and one without.

The experiments reported here evaluated two important aspects related to the use of a denuded MOUDI impactor to collect particulate PAH: a) partitioning of the target PAH between the gas- and the particle-phase, and, b) the effect of the denuder on PAH size distribution measurements.

1. Experimental

Sample Collection: Size-resolved aerosols were collected in Downey, during 24-hr periods, every 7th day, beginning at 8:00 am, during a five-week field campaign, started on September 28, 2000. Samples were collected at 30 LPM using two co-located three-stage MOUDI impactors with three size cuts: < 0.18 μm , 0.18-2.5 μm , and 2.5-10 μm aerodynamic diameter (dp). One MOUDI operated in the “regular mode”, and the other, referred to as “denuded MOUDI”, with a gas trapping system as follows. A 242 mm long XAD-4 coated single-channel annular denuder (URG-2000-30B) was placed upstream of a MOUDI impactor to trap semi-volatile organics while allowing transmission of particles into the impactor. Gas-phase PAHs not retained by the denuder, and any blow off from the impactor stages and the backup filter, were trapped with two polyurethane foam plugs (PUF) placed in series behind the impactor. With this configuration, collection artifacts, if present, may be eliminated or greatly minimized. Immediately after each sampling period, Teflon filters and PUFs were placed in a freezer until they were analyzed.

Except for the last sampling period-- October 26 when it rained-- sampling was conducted under sunny weather conditions. For this reason, data collected on this day were not used to calculate data means.

PAH extraction and Chemical Analysis: Teflon filters corresponding to each size cut, and the two PUF plugs were extracted and analyzed separately by HPLC-Fluorescence methods developed in our lab and reported previously. For every sample, Teflon blanks were run by the analytical procedure and the results used to correct the sample values. The 15 target PAHs, their code and MW are listed in Table 1

Table 1. Target PAHs, Codes, and MW.

	PAH	Code	MW
1	naphthalene	NAP	128
2	acenaphthene	ACE	154
3	fluorene	FLU	166
4	phenanthrene	PHE	178
5	anthracene	ANT	178
6	fluoranthene	FLT	202
7	pyrene	PYR	202
8	benzo(a)anthracene	BAA	228
9	chrysene	CRY	228
10	benzo(b)fluoranthene	BBF	252
11	benzo(k)fluoranthene	BKF	252
12	benzo(a)pyrene	BAP	252
13	indeno(1,2,3-cd)pyrene	IND	276
14	dibenz(a,h)anthracene	DBA	278
15	benzo(ghi)perylene	BGP	276

2. Results and Discussion

Partitioning of the target PAH between the gas- and the particle-phase:

Consistent with literature reports (e.g. Lohmann et al. 2000), the percentage found in the particle-phase generally increases with increasing MW of the PAH (Figure 1). PAHs with MW from 128 (NAP) up to 202 (FLT and PYR) were generally <10% associated with particles. CRY (MW 228) was generally <40% associated with particles, while BAA (also MW 228) $\geq 60\%$ was associated with particles. For MW ≥ 252 they were found predominantly in the particle phase (Figure 1). An adsorptive partitioning model that has been successfully used to predict the gas-particle distribution of SVOCs was developed by Junge (1977) and Pankow (1987)

$$\phi = c\theta / (P_L^o + c\theta)$$

where ϕ is the particle-bound fraction, θ is the particle surface area per volume of air, c is a constant dependent on heat of condensation and surface properties, and P_L^o the PAH subcooled liquid vapor pressure. A literature value for θ used under urban conditions is $1.1 \times 10^{-3} \text{ m}^2/\text{m}^3$ (Junge, 1977) who assumed a value of $c = 0.172 \text{ Pa m}$. Values of ϕ predicted by the Junge-Pankow model for each of the target PAH analytes and for the Downy data (mean of $n=5$ measurements), are plotted in Figure 2. P_L^o values for IND are not available in the literature. As the Figure shows, values of P_L^o are good descriptors of the gas-particle partitioning of PAHs. Considering that this model is based on the Langmuir isotherm and does not take into account the effects of temperature and other atmospheric variables on phase distribution, the measured mean particle-bound fractions (ϕ found for the Downy samples are in reasonable agreement with the predicted model values.

Effects of a Denuder on the PAH Size Distribution: When compared with a regular MOUDI, sampling with a denuder upstream of the MOUDI did not affect significantly the size distribution of the target PAH with higher MW (Figures 3 and 4). Starting with FLT and up to the heaviest target analyte (IND), the distributions obtained with either sampling configuration are quite similar. From BBF to IND, the fraction of mass in the coarse mode is <10%, with both configurations. For these PAHs, most of their mass is associated with particles (Figure 1). For the five PAH with smaller MW, the fraction of mass in the coarse mode was generally higher, reaching 39% for ACE in the denuded MOUDI, and 29% in the regular MOUDI (Figures 3 and 4). The strongest effect of the denuder on the size distribution was seen for

NAP, ACE, and FLU. For PHE and ANT, the fraction of mass in the ultrafine mode was about 10% higher for samples collected with the regular MOUDI.

Summarizing, the use of a denuder upstream of a MOUDI does not significantly affect the size distribution shape and form for ten of the less volatile target PAH (FLT to IND). For the other more volatile PAHs, the differences observed may result from their having very low particle-phase concentrations, making their measurement more difficult.

Mass Balance on Regular vs. Denuded MOUDI:

A mass balance was performed for the target PAHs collected with the regular and the denuded MOUDI. For each case, the mean concentration found in the three stages of each impactor were added (Σ PAHs). As figure 5 shows, the 3-stage Σ PAHs found using the regular MOUDI were higher. Two distinct mechanisms may explain this finding: First, in the denuded MOUDI configuration, when the air exits the denuder, the system is no longer under thermodynamic equilibrium. In this case, the expected result would be desorption of particle-phase PAHs, leading to lower PAH concentrations (a negative artifact). On the other hand, sampling with a regular MOUDI may lead to higher PAH concentrations, due to adsorption of gas-phase PAH on the collection matrices (a positive artifact).

A plot of the ratios of the Σ PAHs obtained using the regular MOUDI to the Σ PAHs using the denuded MOUDI versus the sub cooled vapor pressure is shown in Figure 6. For all PAHs, the concentration ratios varied between 1.0 and 1.5.

4. Conclusions

- Consistent with literature data, the percentage found in the particle-phase increases with increasing MW of the PAH. Particle-bound fractions found for the Downy samples agree reasonably well with the values predicted by the Junge-Pankow model.

- The use of a denuder upstream of a MOUDI does not significantly affect the size distribution shape and form for the ten less volatile target PAH with MW ≥ 202 (FLT to IND). For the PAHs with MW < 202 , the fraction of mass in the coarse mode was generally higher, reaching 39% for ACE in the denuded MOUDI, and 29% in the regular MOUDI. The strongest effect of the denuder on the size distribution was seen for NAP, ACE, and FLU. For PHE and ANT, the fraction of mass in the ultrafine mode generally ~10% higher for samples collected with the regular MOUDI.
- The Σ PAHs found in the 3-stages using the regular MOUDI were higher for all target PAH. This observation is consistent with either a positive artifact for the regular MOUDI, or a negative artifact when using the denuder.

In order to evaluate seasonal and spatial effects, similar experiments will be conducted in Riverside sometime in mid February.

Literature Cited

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Pankow, J. F. *Atmos. Environ.* **1987**, 22, 2275-2283.

Lohmann, R. X.; Harner, T.; Thomas, G. O. and Jones, K. C. *Environ. Sci. Technol.*, **34** (23), 4943 -4951, 2000.

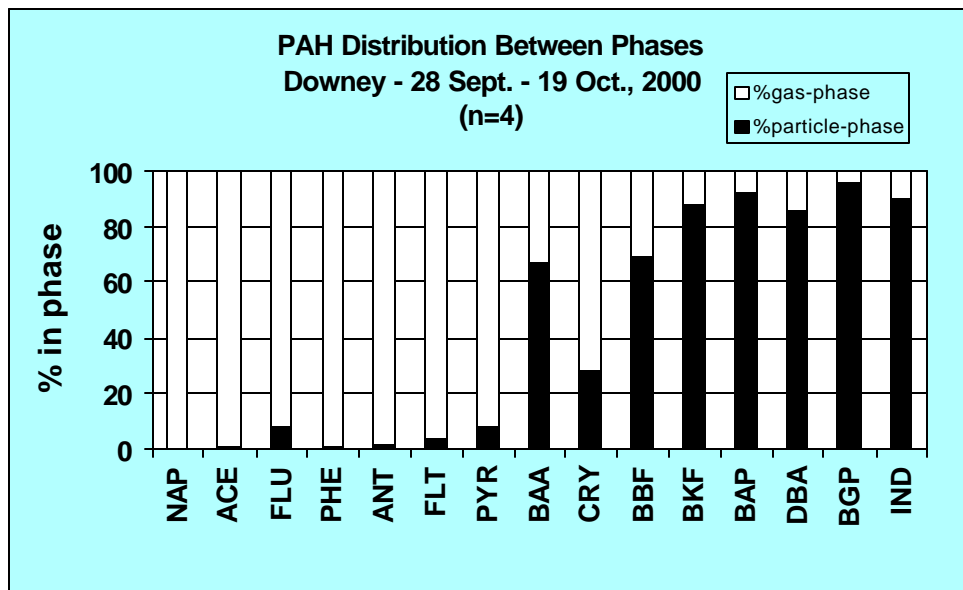


Figure 1. Distribution of PAH between the gas- and the particle-phase. From the lower MW species (NAP) up to (PYR), most of the PAH mass is in the gas-phase. Data from 26 Oct. samples are not included due to raining conditions during sampling.

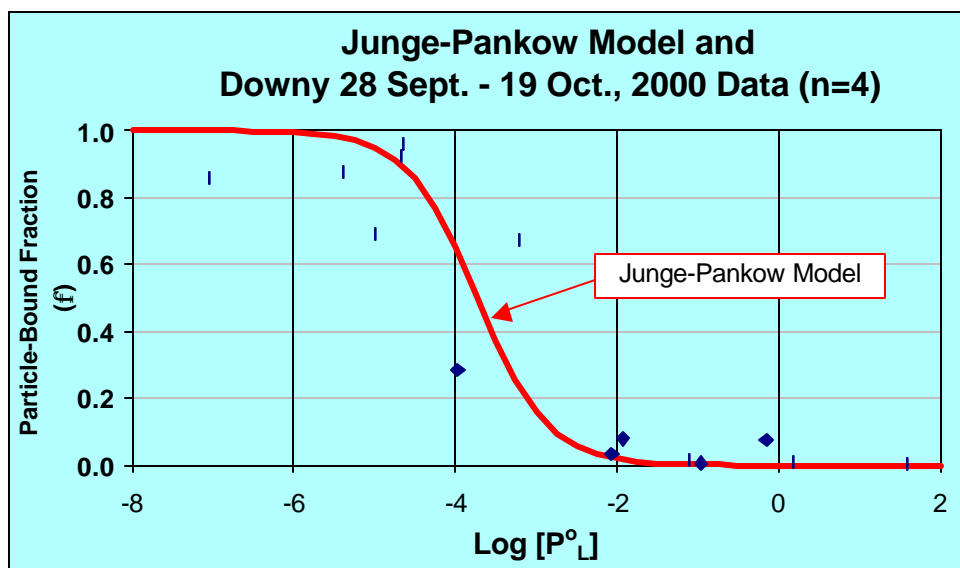


Figure 2. Observed fraction of particle-phase PAHs for Downey samples (mean of n=4 measurements) compared to predictions using the Junge-Pankow adsorption model.

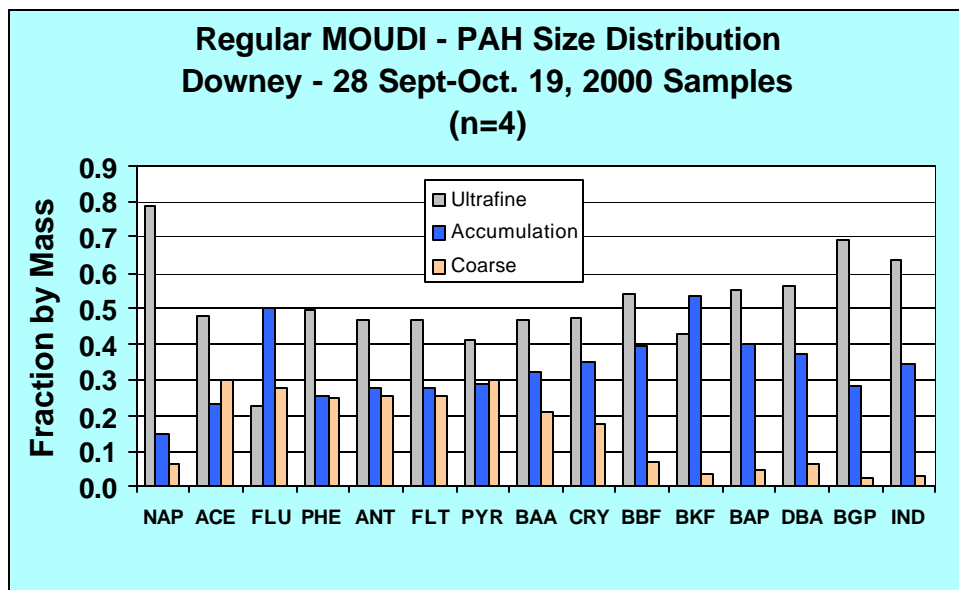


Figure 3. Size distributions means for four samples collected with a regular MOUDI.

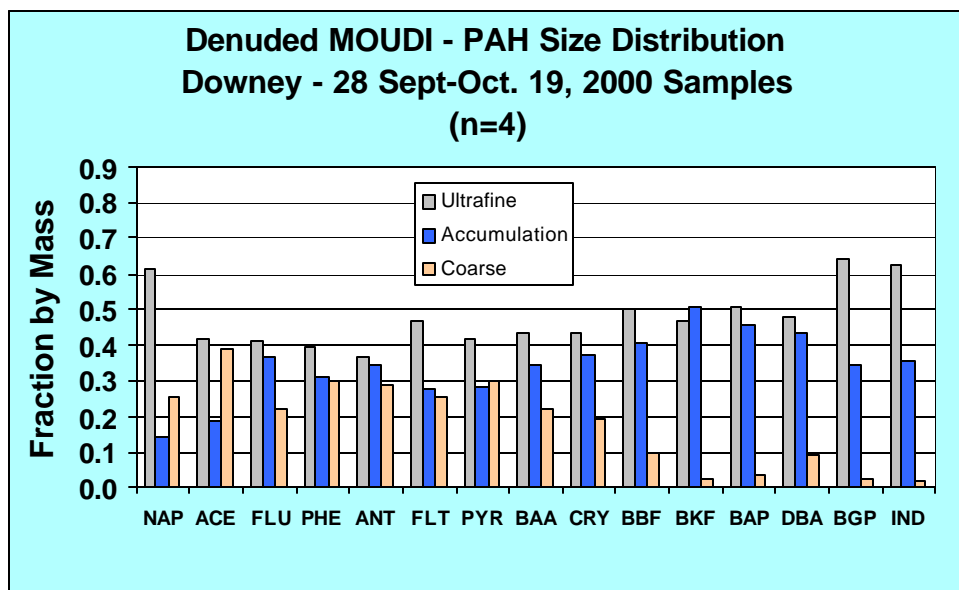


Figure 4. Size distributions means for four samples collected with a denuded MOUDI.

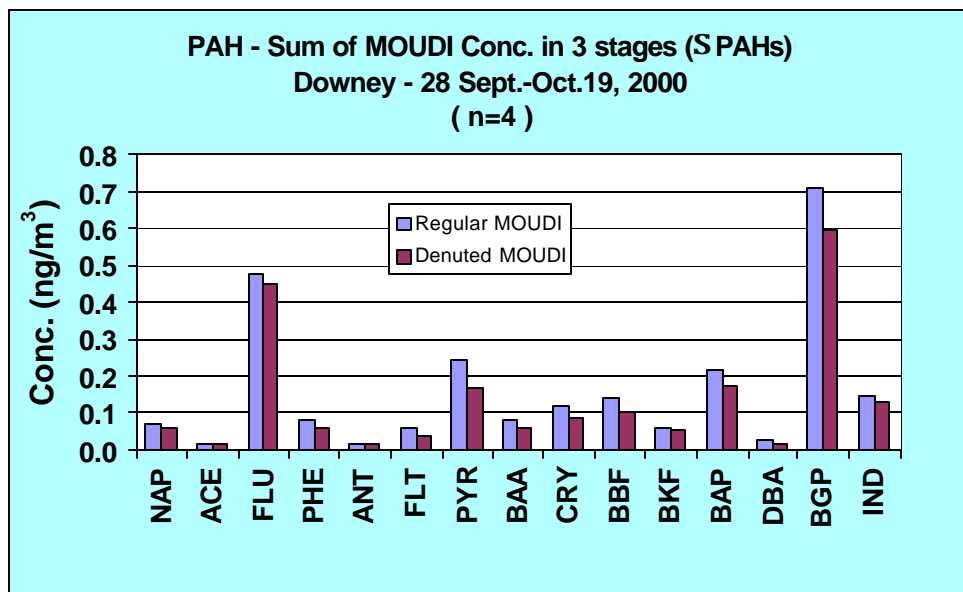


Figure 5. Concentration means for four samples collected with a regular and a denuded MOUDI. For each case, the concentration indicated represents the sum of the concentration values found in the three stages of the impactor.

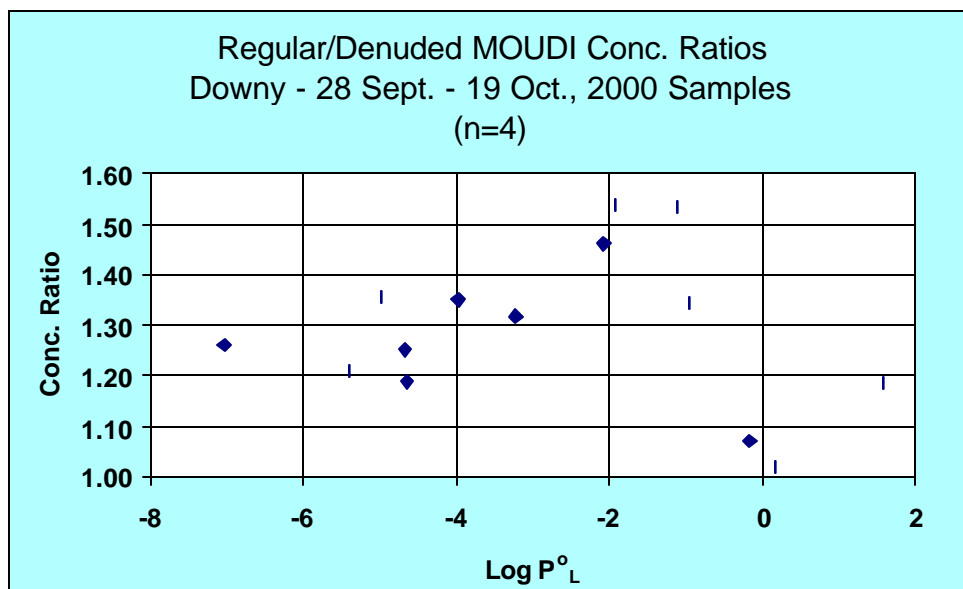


Figure 6. Ratio of the concentration means for four samples collected with a regular and a denuded MOUDI. The concentrations, representing the sum of the concentration values found in the three stages of each

impactor, are shown in figure 5.

6. Investigations of the Concentration and Source Origin of Allergens Present in Airborne Particulate Matter

To refine the characterization of ambient particle material, the biological components need to be identified and quantified. Some bioaerosol constituents, at very low concentrations, elicit health effects. For example nanogram quantities of allergenic proteins generate reactions leading to symptoms ranging from hay fever and asthma to anaphylaxis and death. Among the objectives in the present Supersite project are the determination of spatial and seasonal variations of protein and allergenic material present in airborne particulate matter in the Los Angeles area.

During the present work period, emphasis was given to preliminary experiments to assist in selection of the three Los Angeles area communities for determination of the spatial distribution of protein and allergens. PM₁₀-equivalent particle samples have been collected on 45 mm quartz fiber filters by low-volume sampling (1.4 Lpm) at 13 sites during a 5-year period (1994-1998) as part of the Children's Health Study. The University of Southern California (USC) Children's Health Study is a 10-year epidemiological study of the long-term effects of exposure to air pollution on the respiratory system in children. The 13 communities studied encompass rural coastal areas (Lompoc, Santa Maria, Atascadero), a desert site (Lancaster), mountainous zones (Alpine, Lake Arrowhead), an urban coastal city (Long Beach), down-wind urban sites in the Los Angeles Basin (Glendora, San Dimas, Upland, Mira Loma, Riverside) and Lake Elsinore. Filters, composited by city and a control, consisting of a composite of filter blanks, were extracted with phosphate-buffered saline (PBS), containing protease inhibitors to preserve biological activity of proteins. After filtration through low-protein binding filters (0.22 µm pore size) to remove particles, the extract supernatants were dialyzed against sterile water to remove small molecules (molecular weight cutoff, 3500). Finally, the extracts were concentrated by lyophilization and resuspended to a final volume of 1 mL.

Protein was measured in the 13 sample extracts and the filter blank control extract by two colorimetric protein assays versus bovine serum albumin (BSA) as a protein standard. The Coomassie assay and the bicinchoninic acid (BCA) assay interact with protein in different ways.

The extractable protein levels from airborne particles collected in the 13 Children's Health Study locations were much lower than expected. When determined by the BCA assay, the total protein concentrations were found to be in the range of 0.016 to 0.041 $\mu\text{g m}^{-3}$, except for Mira Loma, where the BCA assay suffered from interferences and had to be replaced by an alternate assay technique. The lowest protein concentrations were found in the rural coastal areas, Lompoc, and Santa Maria. The highest protein concentrations were found in the eastern area of the Los Angeles Basin (Glendora, Upland, Riverside, Mira Loma). The absolute values of the protein concentrations found at the Children's Health Study locations are lower than for our previously published results for Long Beach, downtown Los Angeles and Rubidoux, for composites of samples collected from October 1994 through May 1995. One possible reason for the low protein yields could be partial inactivation or degradation of the protein on the filters during the many years of storage of the Children's Health Study samples prior to extraction. Never the less, indications are that there are higher absolute protein concentrations in the air in the eastern LA basin than in the less populated and better ventilated coastal areas, and this knowledge will help with siting decisions for the next round of atmospheric sampling.

The next big aim in the allergen project is to prepare for collection of larger quantities of fresh atmospheric particulate matter at three of the Children's Health Study sites by sampling with high-volume PM_{10} samplers. An attempt will be made to measure the total allergen binding activity in the extracts from each of the historical Children's Health Study sample composites in order to help choose the three sampling sites. Three PM_{10} high-volume samplers have been delivered and will be assembled and calibrated. Sampling should begin within the next quarter.

7. Development of a New High-Quality Continuous Coarse PM Monitor

Measurement of coarse PM are inherently more complex and less precise than direct measurements of either PM_{2.5} or PM₁₀ made with continuous or time-integrated monitors, as they are measured by the difference between collocated PM₁₀ and PM_{2.5} samplers. Depending on the measurement method, PM_{2.5} to PM₁₀ ratios and actual coarse PM concentration, mass concentration data for coarse PM may be substantially less precise than those for PM₁₀ or PM_{2.5}.

As part of our Methods development section of our Supersite activities, we have developed a monitor that will yield precise, accurate, artifact-free coarse PM concentrations near-continuously (i.e., in intervals of 5 minutes or less). This technology and its performance evaluation is described in greater detail in manuscript that we submitted for publication to the *Journal of Air and Waste Management Association* (DEVELOPMENT AND EVALUATION OF A CONTINUOUS COARSE (PM₁₀ - PM_{2.5}) PARTICLE MONITOR, Chandan Misra, Michael D. Geller, Pranav Shah, Constantinos Sioutas and Paul A. Solomon). This work was also presented to the Technical Subcommittee of the Clean Air Scientific Advisory Committee (CASAC) on Particle Monitoring in January 22, 2001 at RTP.

The operating principle of the monitor is based on enriching coarse particle concentrations by a factor of about 25 by means of a sharp 2.5 μm cutpoint virtual impactor (USC Dichotomous Sampler), while maintaining fine PM at ambient concentrations. The aerosol mixture is subsequently drawn through a standard TEOM, the response of which is dominated by the contributions of the coarse PM, due to concentration enrichment.

The continuous coarse particle monitor, shown schematically in Figure 7, operates at an intake flow of 50 LPM, and consists of three main components: a) a PM₁₀ inlet; b) a 2.5 μm cutpoint virtual

impactor (or, coarse particle concentrator), and; c) a R&P TEOM (Model 57-000596; Rupprecht and Patashnick, Albany NY).

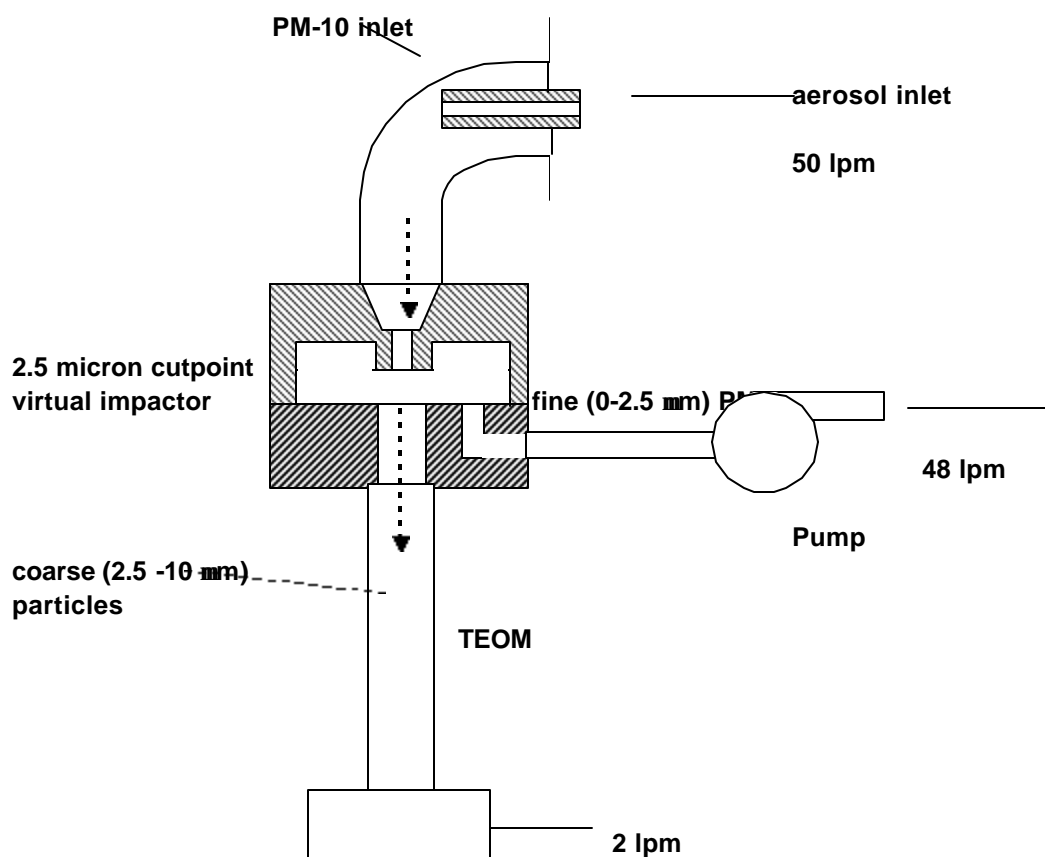


Figure 7. Schematic of the Continuous Coarse Particle Monitor

Findings from the field study ascertain that a TEOM coupled with a PM10 inlet followed by a 2.5 μm virtual impactor can be used successfully for continuous coarse particle concentration measurements. The average concentration-enriched TEOM coarse concentrations were approximately 26-27 times

higher than those measured by the time-integrated PM₁₀ samplers (MOUDI and Partisol Dichotomous sampler), and highly correlated, as shown in Figures A22-A23. Coarse particle concentrations measured by the concentration-enriched TEOM were independent of the ambient fine-to-coarse PM ratio (Figure A24).

During these experiments, ambient PM data for a few selected runs were recorded using an APS. Figure A25 shows the time series in coarse PM mass concentrations measured by the TEOM and the APS during one day of the field experiments. The TEOM coarse particle concentrations were converted to ambient CM by dividing by 26. Direct comparison between the actual concentrations measured by the two monitors can not be determined, since the density of ambient coarse particles is required to convert the APS volume concentrations to mass concentrations. However, as the data plotted in Figure A25 clearly show that excellent overall agreement is observed in the time trends of the two samplers.

7b. Comparison Between the PM_{2.5} and Coarse (PM₁₀ – PM_{2.5}) concentrations between the MOUDI and Partisol

As part of the field evaluation of the continuous coarse monitor, the PM₁₀, coarse, and PM_{2.5} concentrations obtained by means of the MOUDI and Partisol samplers were compared. It should be noted that several of these field experiments were conducted under conditions of unusually low ambient relative humidity (RH), even by the standards of the generally arid climate of the Los Angeles Basin, often below 20 to 30 %. From the data plotted in Figure A26, there is a well-defined inverse relationship between this ratio and the RH. This ratio achieves an ideal value of 1 as the RH reaches 45-50 %. For lower RH, this ratio increases sharply and becomes as high as 5 when the RH reaches the 10 to 15% range.

To confirm that this phenomenon is related to particle bounce, which would be more pronounced at lower RH, the ratio of fine PM concentration of Dichotomous Partisol-to-MOUDI vs RH was plotted, as shown in Figure A27. The reverse trend is observed, with the ratio of the fine PM of the

Dichotomous Partisol-to-MOUDI increasing from 0.2 to about 1, as the RH increases from 10 to 50 %. Further, the total PM₁₀ Dichotomous Partisol-to-MOUDI ratio was 0.99 (\pm 0.13) based on 30 field experiments, thereby suggesting that since both samplers agreed well for PM₁₀, the only difference is in the fine and coarse particle measurements, that is, coarse PM is low and fine PM is high at low RH, suggesting particle bounce. These field observations illustrate one of the main drawbacks of impactors, and raises serious implications on the appropriateness of using impactors with uncoated substrates to obtain the size distributions of aerosols under low (< 30%) RH conditions.

7c. Relationship Between the Fine -to-Coarse PM ratio and Coarse PM Mass Median Diameter (MMD)

During the evaluation of the performance for the continuous coarse PM monitor, we determined size distributions of coarse ambient particles by means of the APS, since we assumes that the average coarse PM size , expressed by the MMD, would affect the response of the continuous coarse monitor. Our experiments indicated that the coarse MMD decreases as the fine-to-coarse PM concentration ratio increases (Figure A28). There is a marked shift in MMD from 4.8 – 5 μ m to 2.8 – 3 μ m as the ratio of fine-to-coarse PM concentration increases from 1 to 5 respectively.

The highest values of fine-to-coarse PM concentrations, ranging from about 3.5 to 4.6, were obtained on October 20 to 21, 2000. During these two days, stagnation conditions occurred in Downey, with the average wind speed during the sampling periods being less than 1 mph. Two-hour averaged fine PM concentrations measured by either the MOUDI or Partisol during these two days ranged from 80 to 146 μ g/m³. These conditions are expected to result in high fine PM concentrations in locations such as Downey, which is primarily impacted by vehicular emissions from nearby freeways, while the relatively low coarse PM concentrations may be explained by the lack of sufficient wind velocity to either generate or transport coarse particles.

These investigations will continue in our next Supersite site, at Riverside, CA and the relationship between coarse-to-fine PM concentrations, coarse PM MMD and wind speed and direction will be investigated more systematically.

8. *Size-segregated on-line measurement of particulate carbon, nitrate and sulfate using the Integrated Collection and Vaporization Cell*

The ADI Integrated Collection and Vaporization Cell (ICVC) is an automated collection and analysis method for high-time resolution determination of the major chemical constituents of ambient particles. Particles are collected onto small (approx 1 mm dia) area on a solid substrate, and then assayed in place by rapid heating of the substrate and analysis of the evolved vapors. Different chemical constituents are determined through the selection of the heating conditions and the vapor analyzer. For nitrate analysis, the heating is done at low temperatures in a nitrogen atmosphere, and the evolved vapors are quantitated with a chemiluminescent nitrogen oxide analyzer operated with a MgO catalyst that reduces higher nitrogen oxides to nitric oxide. For sulfate the analysis uses a high-temperature heating in air, with detection using a fluorescence SO₂ analyzer. For carbon we use an NDIR detector to quantitate the evolved CO₂. The analysis step is just under two minutes. Typical collection periods are eight minutes. Overall cycle time is 10 minutes.

Efforts for the Los Angeles Supersite program have focused in two areas: (1) the improvement of the quantitation of the analysis for particulate carbon, and (2) the design and characterization of the size-segregating collection and analysis system. The analysis of carbon requires conversion of the evolved organic vapors to carbon dioxide. Two steps have been taken to improve the carbon recovery. First, we now use a platinum substrate, which improves the vaporization of the soot-like carbon from the substrate. Secondly, we added a quartz oven at 650C with a MnO_2 catalyst to convert the evolved vapors to CO_2 . This has given us equal responses for standards of potassium bithalate and oxalic acid mixed with ammonium sulfate. Recoveries are 90% of theoretical. Currently we are exploring the use of a TiO_2 catalyst that is activated by ultra-violet light rather than requiring heating.

The current ICVC system collects fine particles in one stage, yielding a single $\text{PM}_{2.5}$ particle sample for analysis of the sulfate, nitrate and carbon concentrations. For the size resolved analysis of these chemical constituents a cascaded ICVC will be used, as shown in Figure 8. Additions to the single-stage ICVC include active control for the humidifier, cascaded collection cells, and active control of the analysis gas flows. The humidifier is needed to wet the particles so that they adhere upon impaction. Yet for sizing, excessive humidification must be avoided. Target humidification to meet these needs is 75+-5%. To achieve this we plan to use a feedback system that controls the absolute pressure of saturated vapor in the annular region of a Nafion dryer (D. Collins, personal communication). The individual stages are then cascaded, and samples from each stage are analyzed in place. The cascading is possible because the ICVC technique does not require valving-off the sample line for analysis. Instead, the majority of the analysis carrier gas is introduced into the cross flow of the target cell which

is also open to the analyzer. Isolation is provided by bleeding additional carrier gas into the cells or lines immediately above the target cell. To achieve the proper balance, control of the cross flow is needed so that the proper flow ratio is drawn into the analyzer. Efforts to date have focused on the active control of this cross flow.

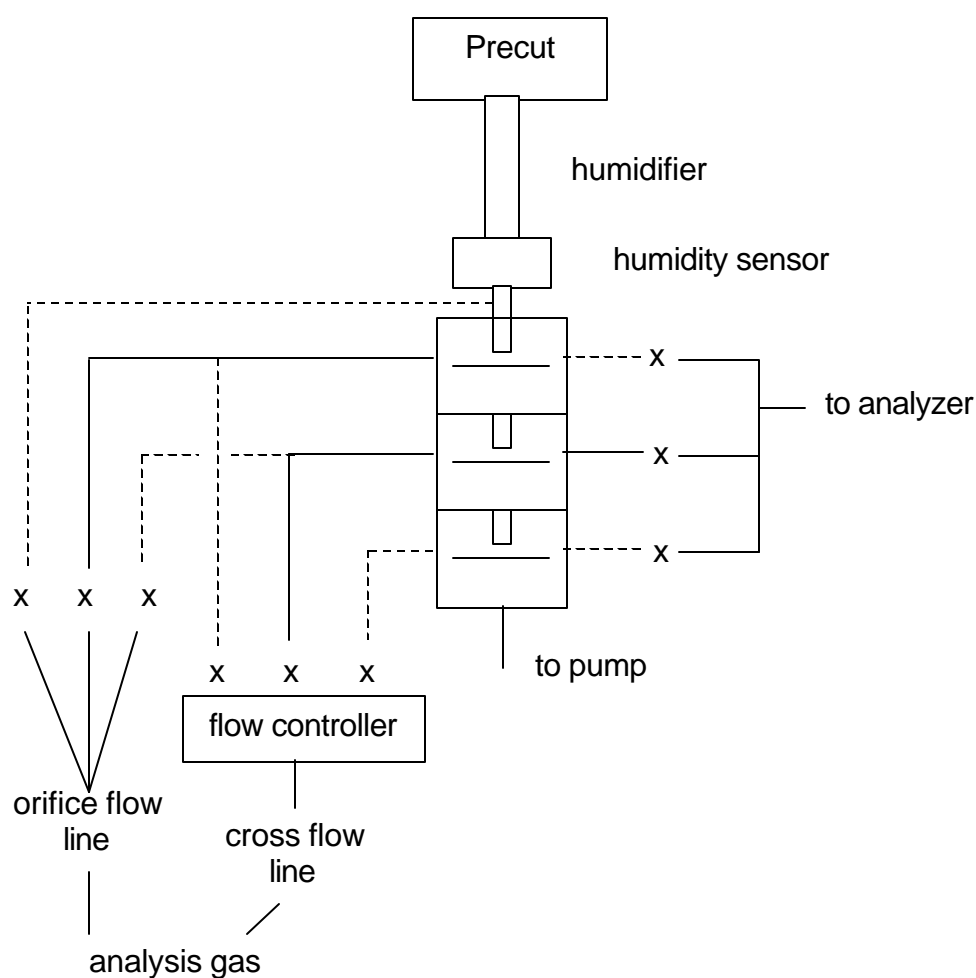


Figure 8. Schematic of the cascaded ICVC for size-resolved analysis of sulfate, nitrate or carbon. Solid lines show those analysis carrier gas lines that are active for the analysis of the middle stage.

9. Progress on Site identification

A key feature of our Supersite activities was the ability to conduct state-of-the-art measurements of the physicochemical characteristic of PM in different locations of the Los Angeles Basin (LAB).

We have proposed a 2.5-year repeating cycle of measurements at five locations. Each location will be sampled during a period of intense photochemistry (defined approximately as May – October) and low photochemical activity (defined as the period between November – April). We have identified the following 7 locations as ideal candidates for the principal Supersite sites. These are:

- 1.Rancho Los Amigos Medical Center (Alameda Corridor)
- 2.Long Beach (coastal site)
- 3.Rubidoux (eastern region, SCAQMD speciation site)
- 4.Azusa (SCAQMD PM monitoring site; inland valley)
- 5.Riverside (eastern region site, operated by University of California Riverside)
- 6.Boyle Heights (site immediately downwind of vehicular emission sources)
- 7.Upland/Claremont (eastern region, receptor site).

The last two sites were added to our original 5 candidate sites because recent data from Cass et al (CRC Project No. A-22 - Final Report; Characterization and Evolution of Primary and Secondary Aerosols During PM_{2.5} and PM₁₀ Episodes in the South Coast Air Basin) indicate that the U.S. 10 freeway lies on a trajectory primarily impacted by mobile source emissions. The Boyle Heights, Azusa and Upland sites fall within the “vehicular emissions” trajectory that is tangential to freeway 10. The Long Beach, Downey, Riverside and Rubidoux sites fall along a different wind trajectory that is called “Nitrate-Oriented Trajectory”. This trajectory starts in the Long Beach area, where PM is mostly generated by petroleum refineries, numerous energy generating facilities and heavy industry emission, and progresses through areas that are upwind of, within, and downwind of the Chino dairy area, a large source of gas-phase ammonia. Our plan for the next 4 years is to visit each of the 3 sites along each trajectory during a period of high and low photochemical intensity.

Sampling in our Rancho Los Amigos has been completed and we are currently in the process of disassembling our PIU, which will be deployed to Riverside, our second principle Supersite site. Installation and set-up at Riverside, including power hook-up has been scheduled for February 13, 2001. We anticipate staying in Riverside until the end of May, 2001, by which time we will move to Rubidoux for the months of June, July and August 2001. Starting September 2001 we will move to Claremont/Upland, where we will spend the next 4-5 months. Finally, in the winter of 2002 we will move to Azusa. It should be noted that this is a tentative plan and it may be subject to changes, depending on the needs of our PM Center investigators who will be using these data.

Consistent with our original proposal, we are currently in the process of characterizing PM and gaseous co-pollutants as a function of distance from a freeway. Towards this goal, we have identified and secured an ideal site, at Boyle Heights. The specific site is located about 1 mile east of downtown LA, in the parking lot of the East LA Technology Center of the LA Unified School District. The site is downwind of Freeway 5 and is located 15-20 meters away from the freeway. Quiet side streets, perpendicular to freeway 5, will enable us to conduct our measurements (in conjunction with inhalation exposure studies to concentrated PM from the freeway, utilizing the USC particle concentrators) in discrete distances from that freeway.

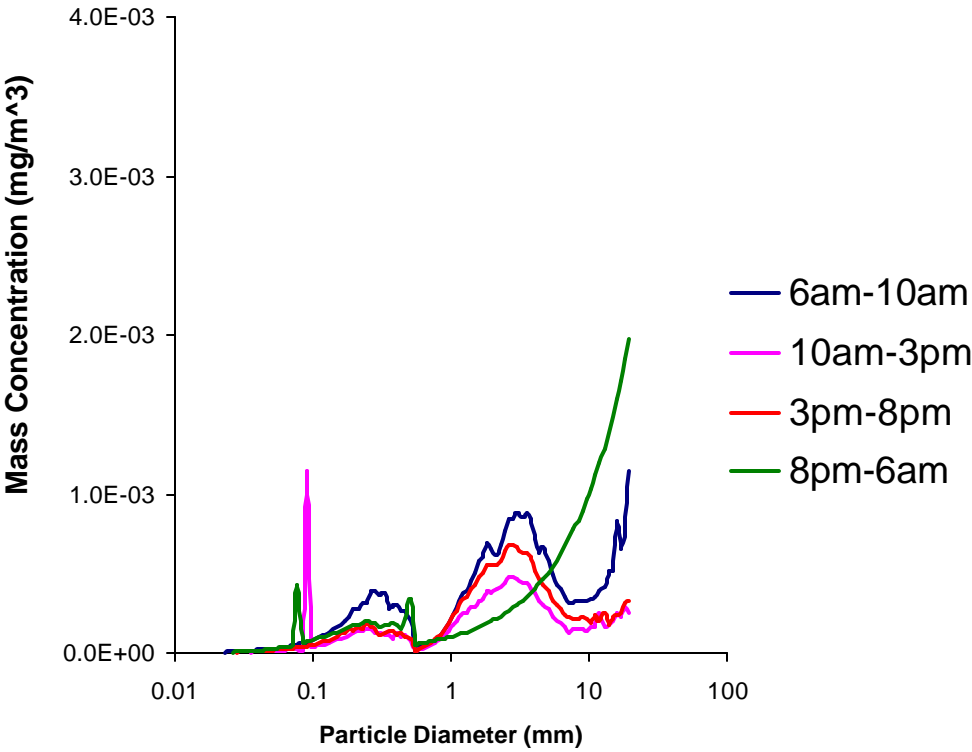
We have already secured the sites of Riverside, Rubidoux, Long Beach, Azusa and Boyle Heights. We are in the process of investigating different options for placing our PIU and concentrator trailers in the Upland/Claremont area and we expect to finalize our last site in that area within the next 2-3 months.

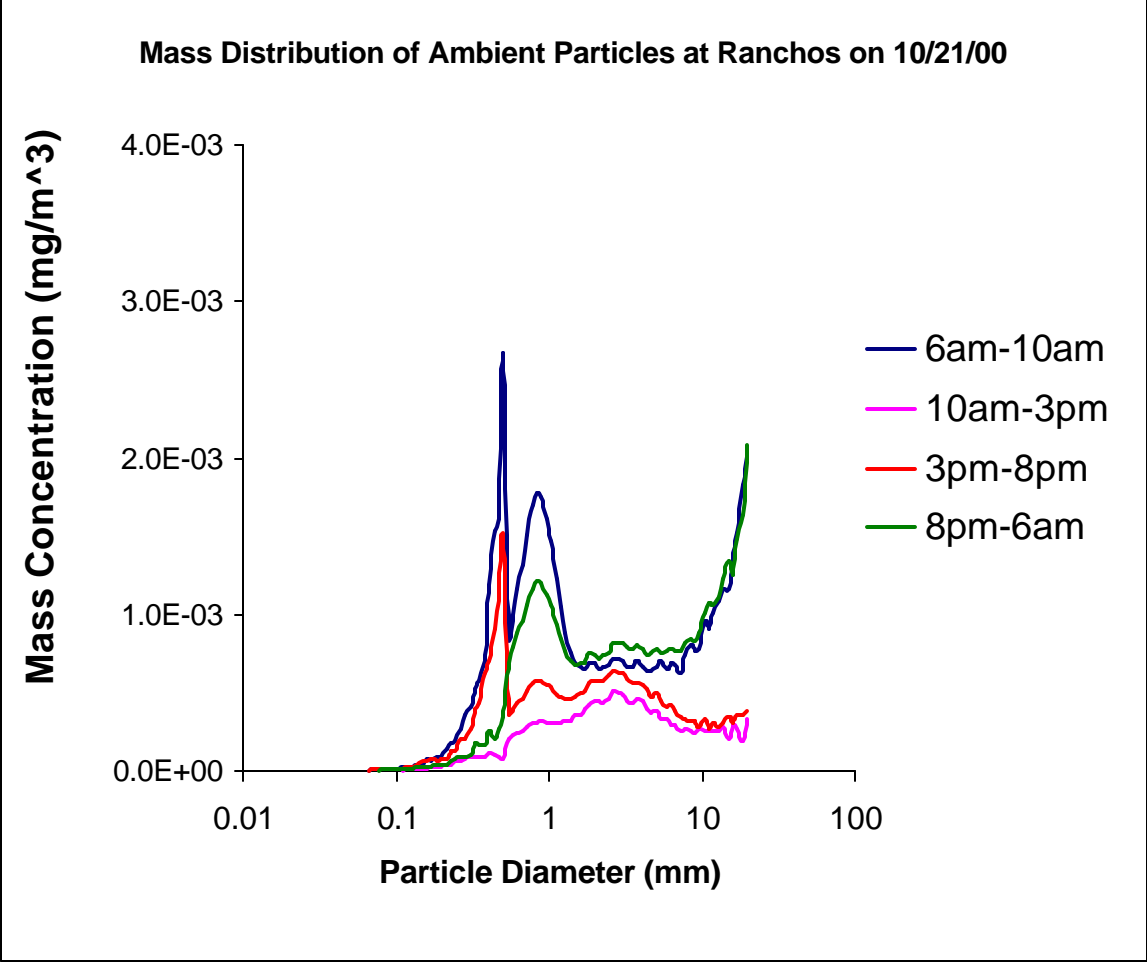
In both the Long Beach and Boyle Heights sites, we will coordinate our measurements with those conducted by ARB, which focus on measurement of air toxics in environments where children spend the majority of their time (funding for these monitoring activities comes from Senate Bill 25). Our activities will be thus leveraged with the concurrent ARB measurements, which will provide us with information on organic air toxics (mainly in the vapor phase) currently not measured by our Supersite, but which are important in supporting the toxicological and in vitro evaluation health studies that we will be conducting in our Supersite locations.

10. Progress with Quality Integrated Work Plan (QIWP)

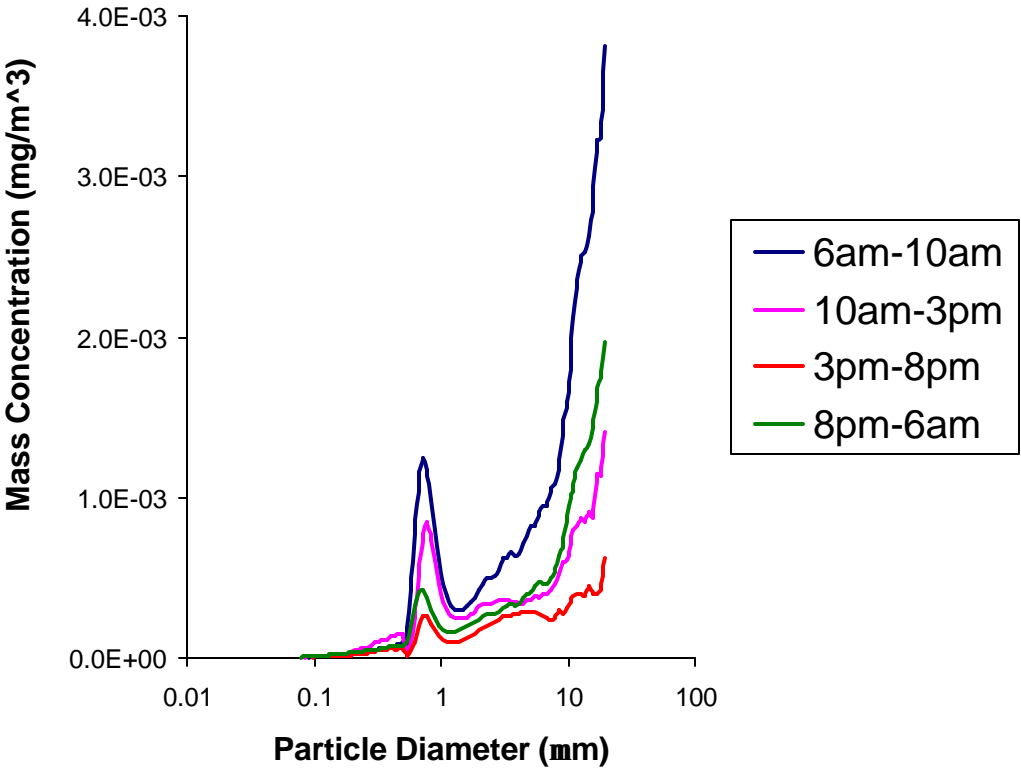
Our Quality Integrated Work Plan (QIWP) was submitted to EPA on January 31, 2001. We expect that some minor modifications will be made as we move along with each of our projects and as we keep refining the operation procedures and learn from our experiences. The document has been sent to the Office of Air Quality Planning and Standards Emissions, Monitoring and Analysis Division for approval and recommendations.

Mass Distribution of Ambient Particles at Ranchos
on 10/10/00

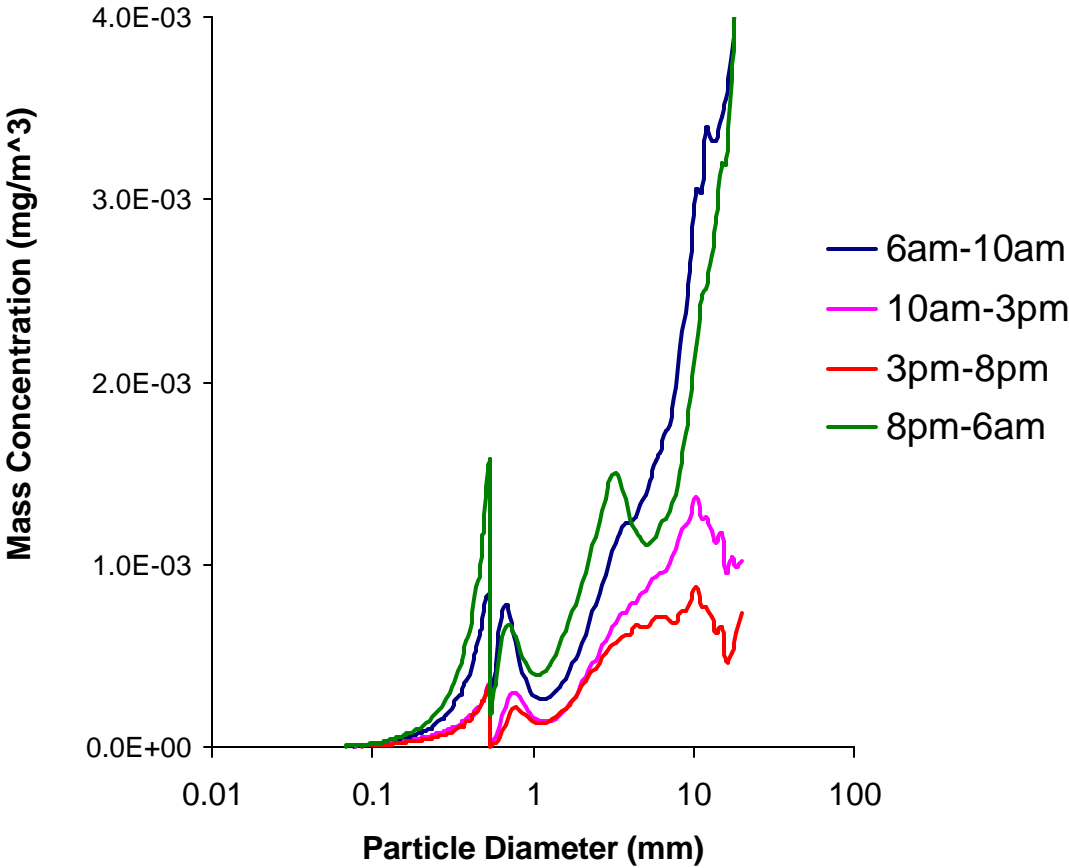




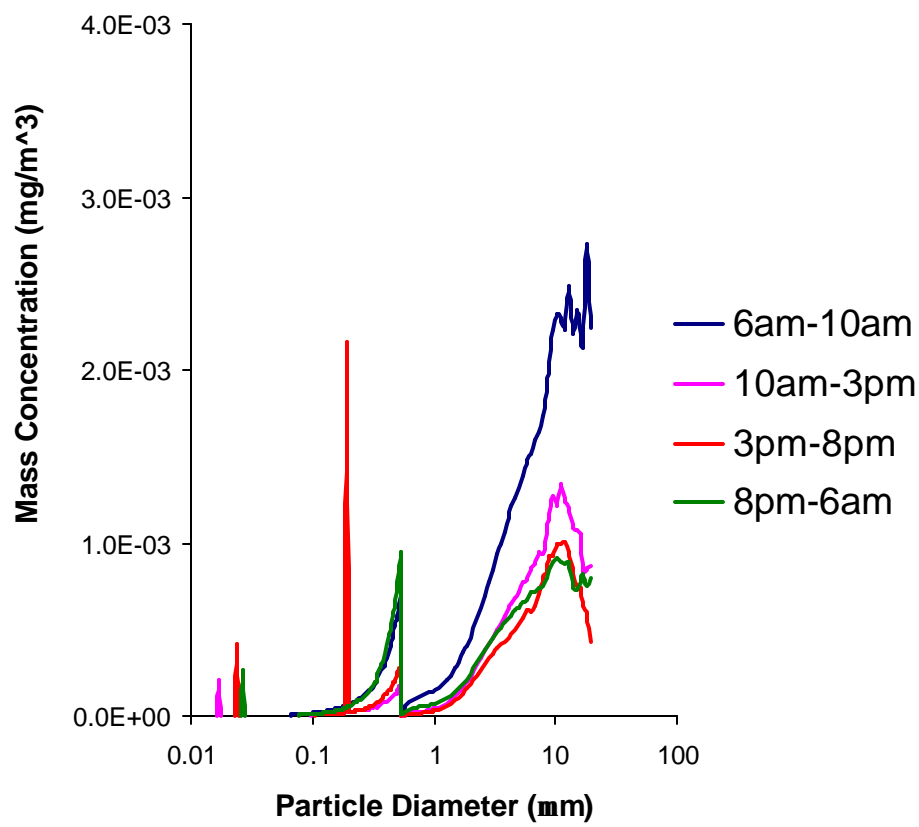
Mass Distribution of Ambient Particles at Ranchos on
12/08/00

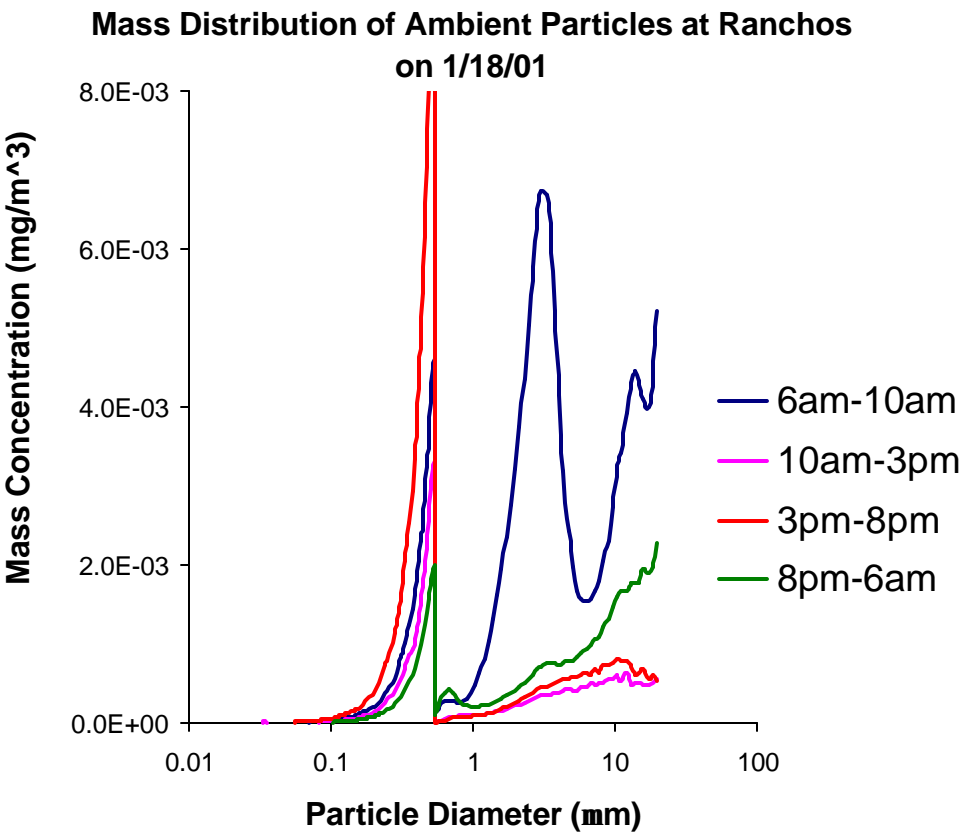


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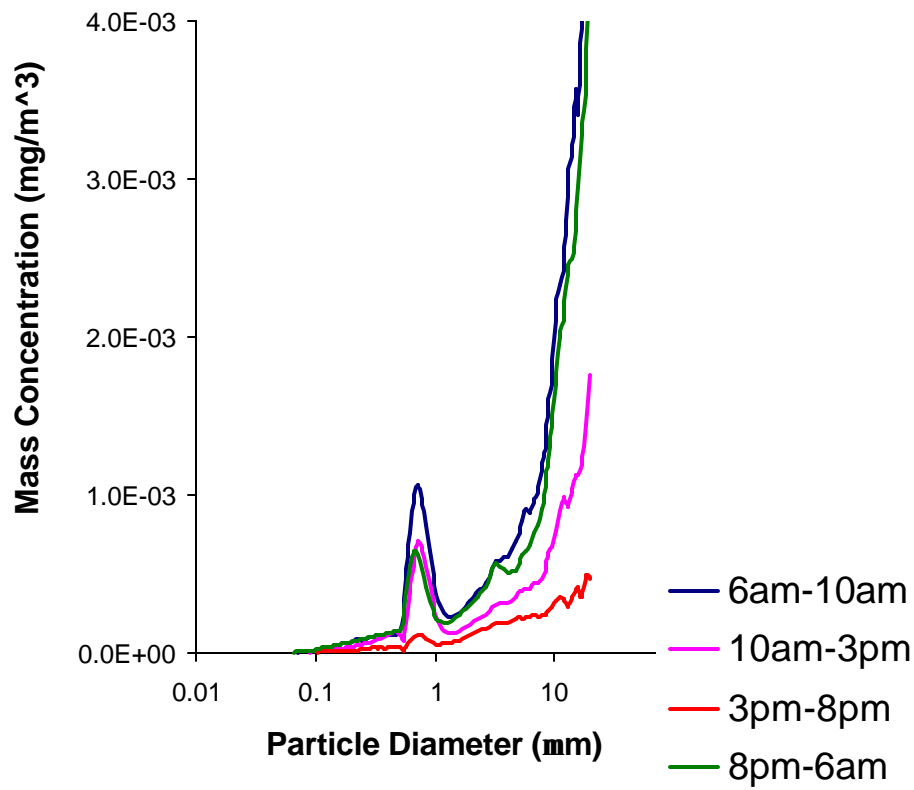


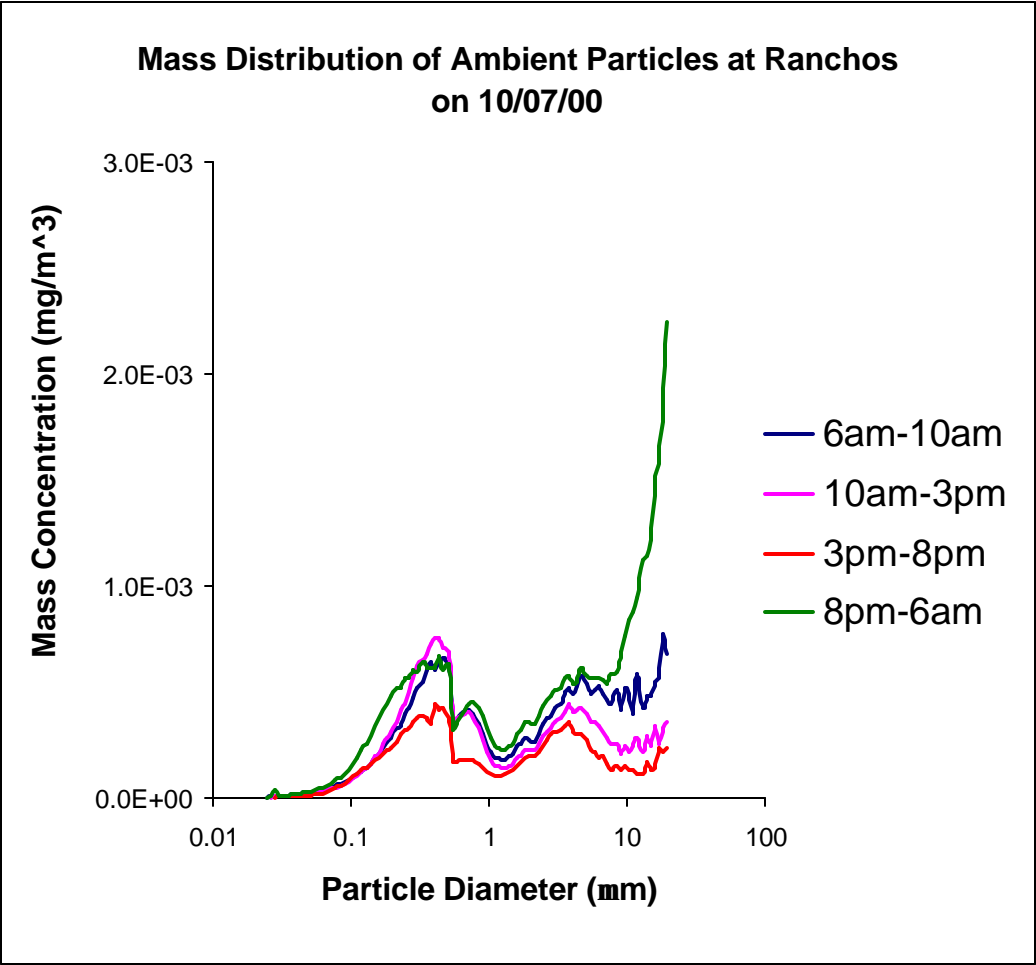
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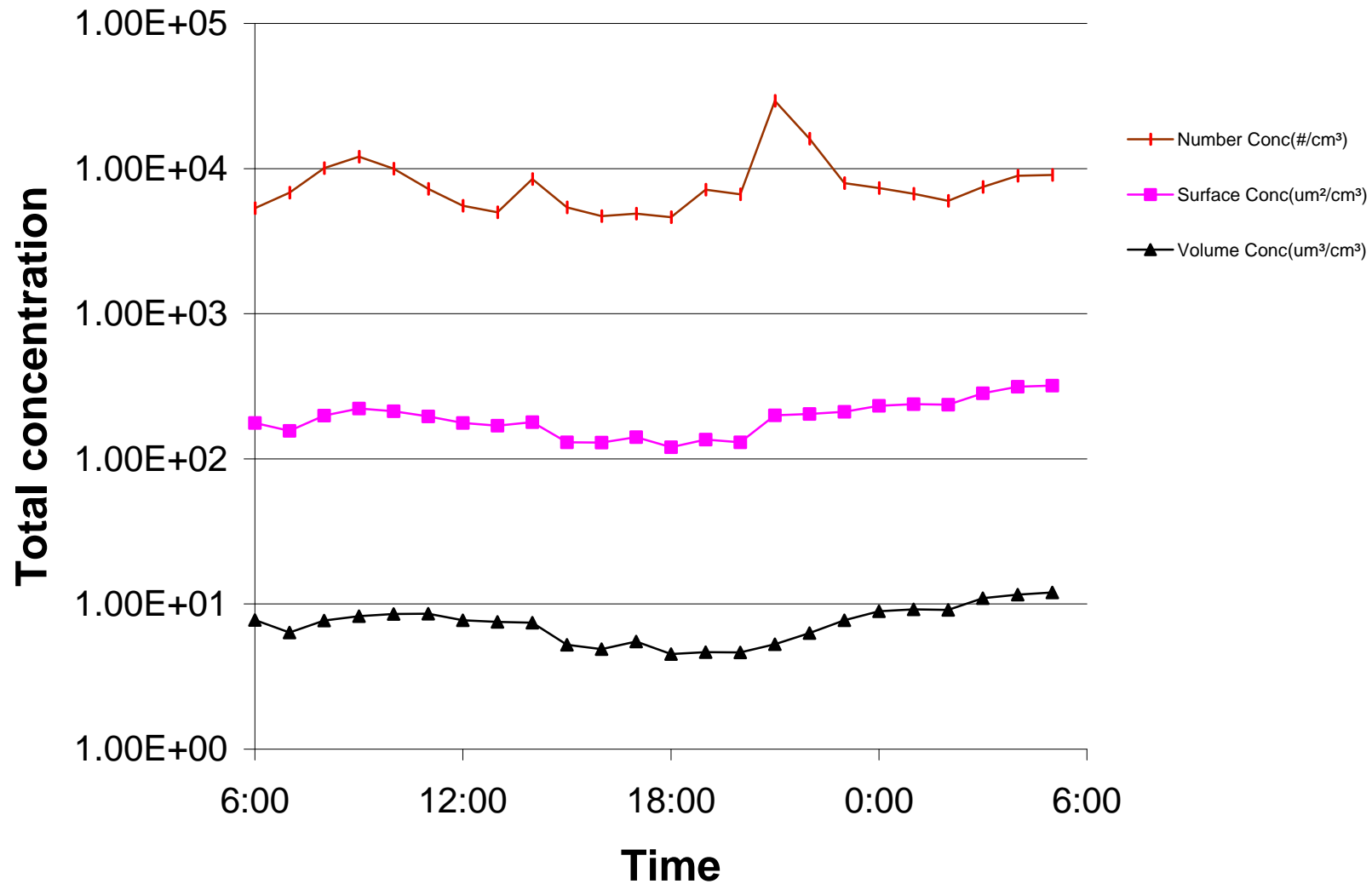


Mass Distribution of Ambient Particles at Ranchos
on 12/10/00

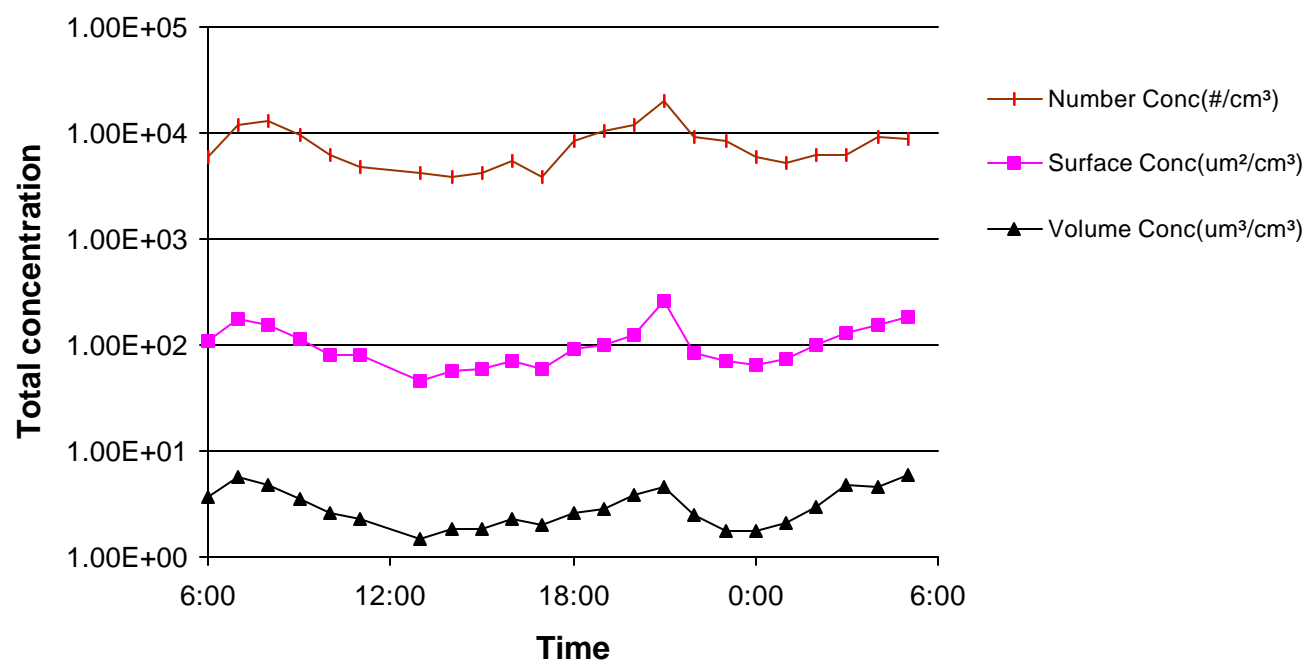




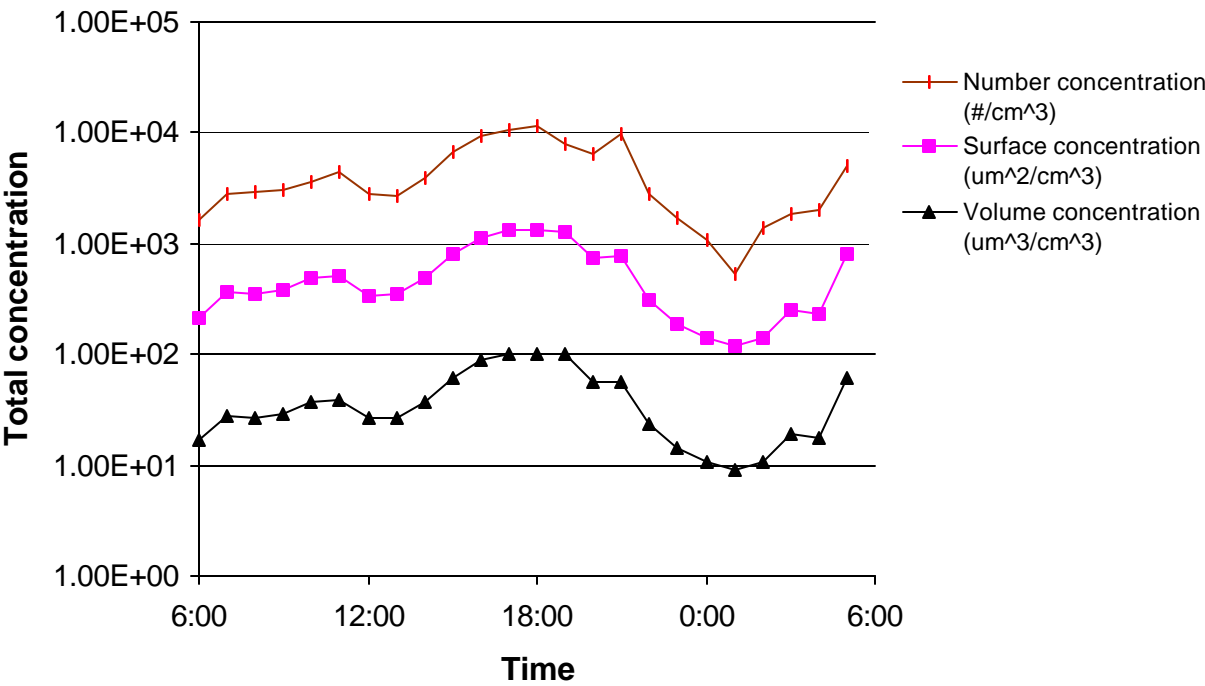
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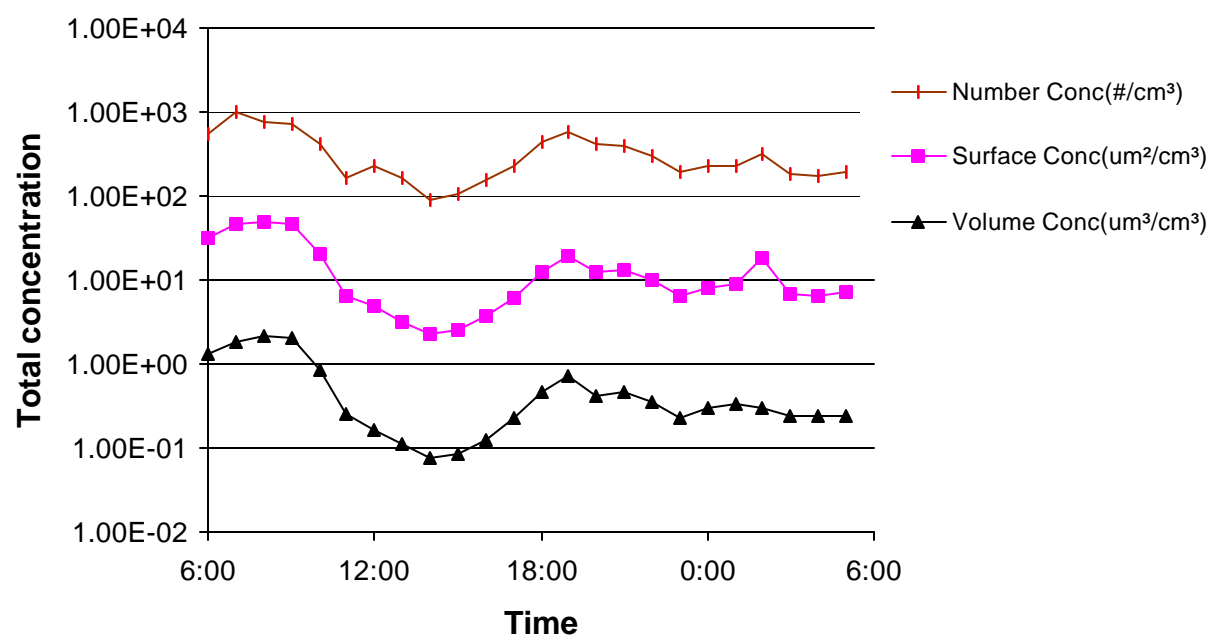
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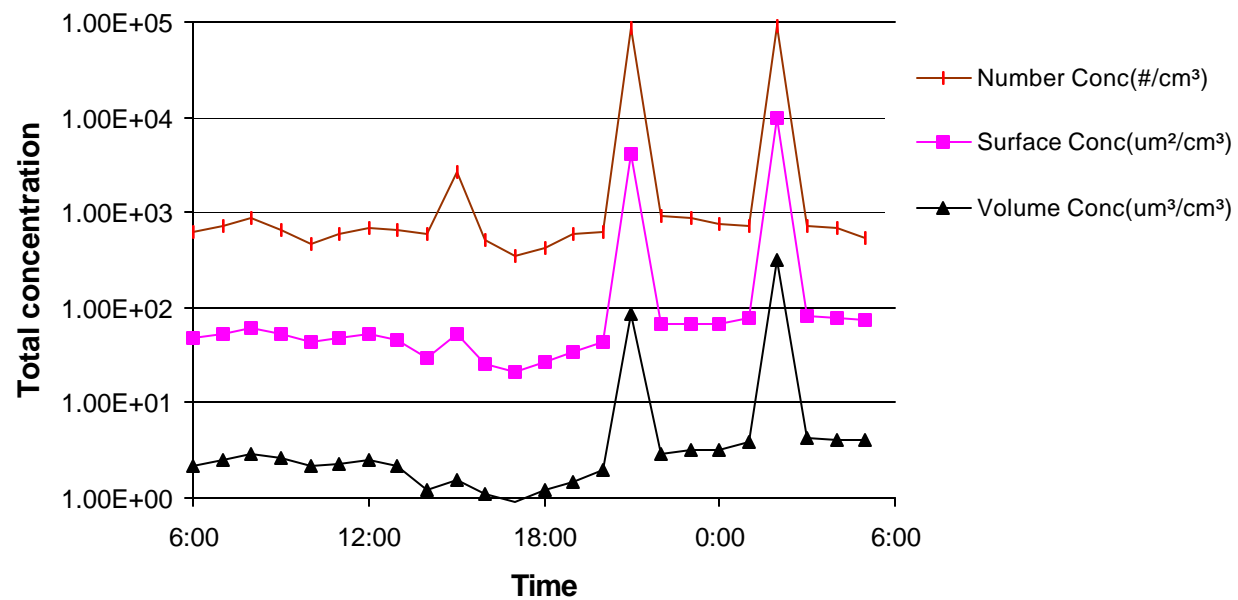
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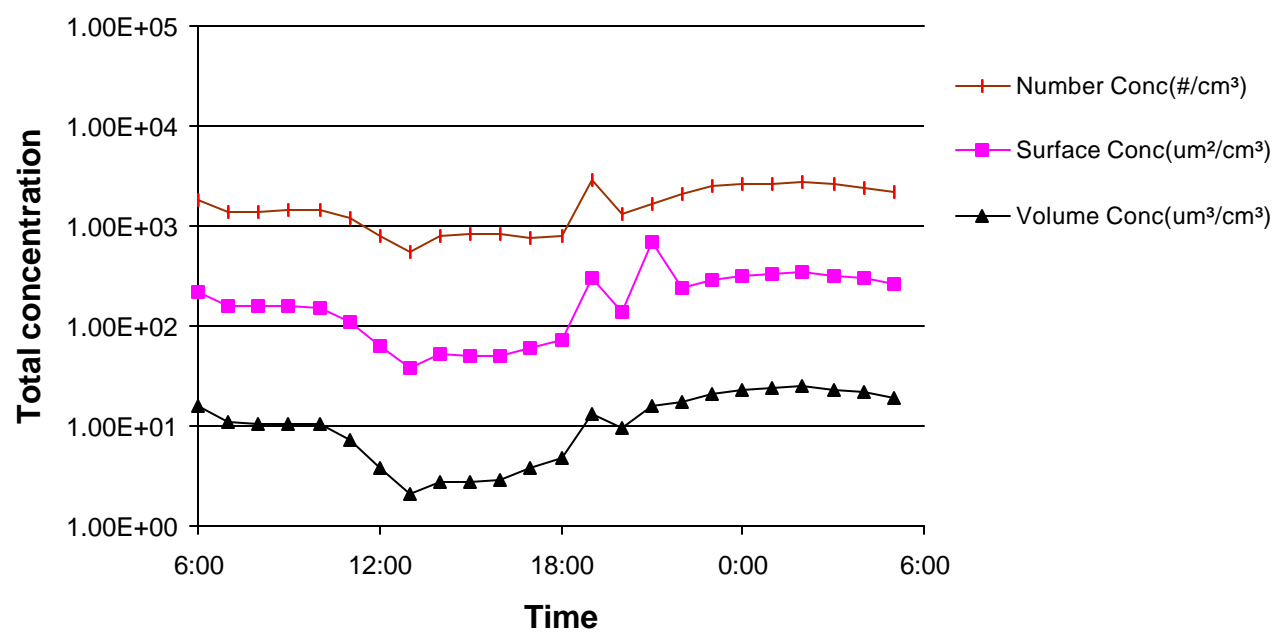
**Total concentration of ambient particles at Rancho Los Amigos
on 12/10/2000**



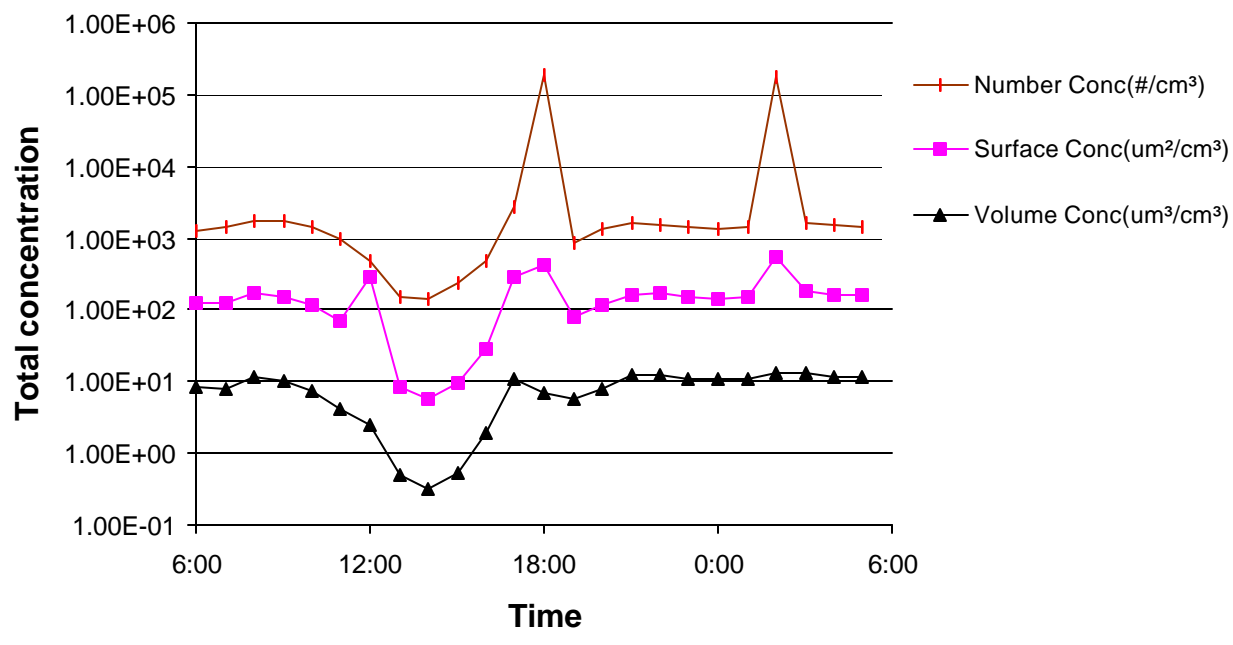
**Total concentration of ambient particles at Rancho Los Amigos on
12/08/2000**



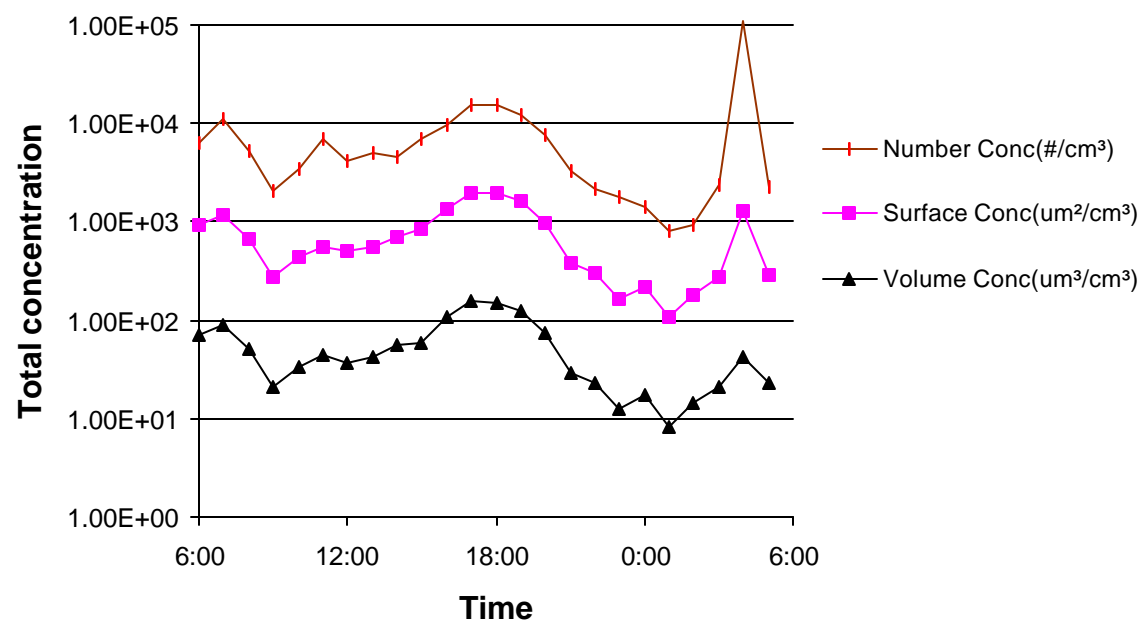
**Total concentration of ambient particles at Rancho Los Amigos on
12/29/2000**



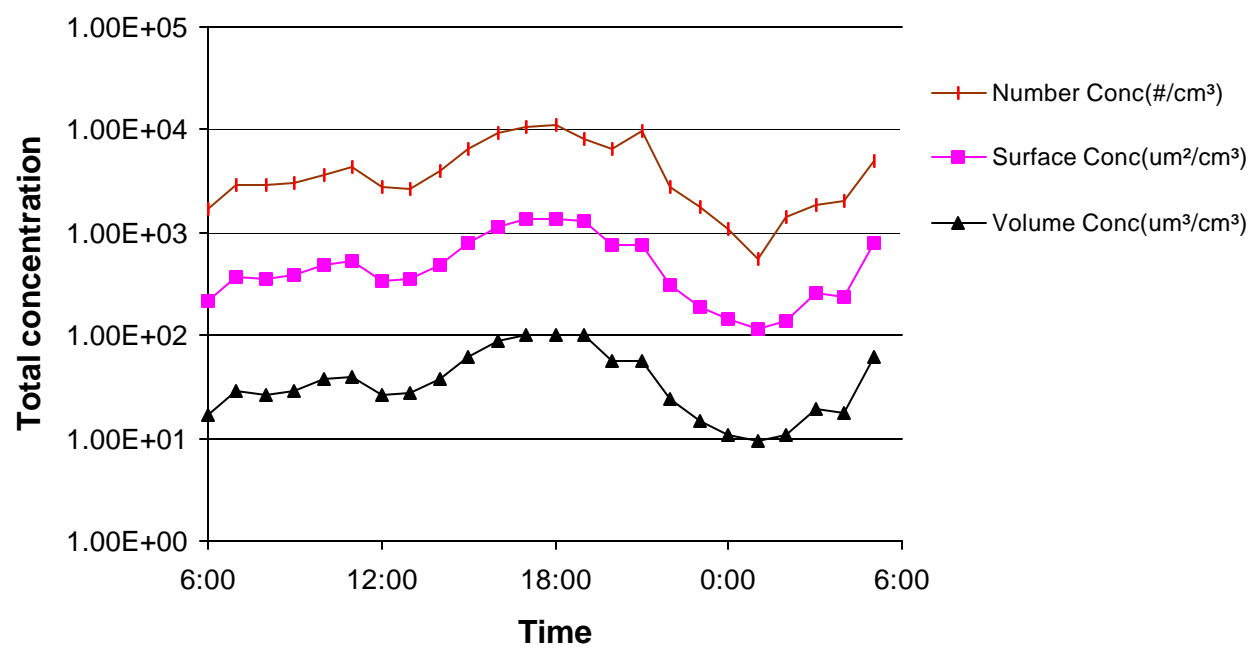
**Total concentration of ambient particles at Rancho Los Amigos
on 1/3/2001**



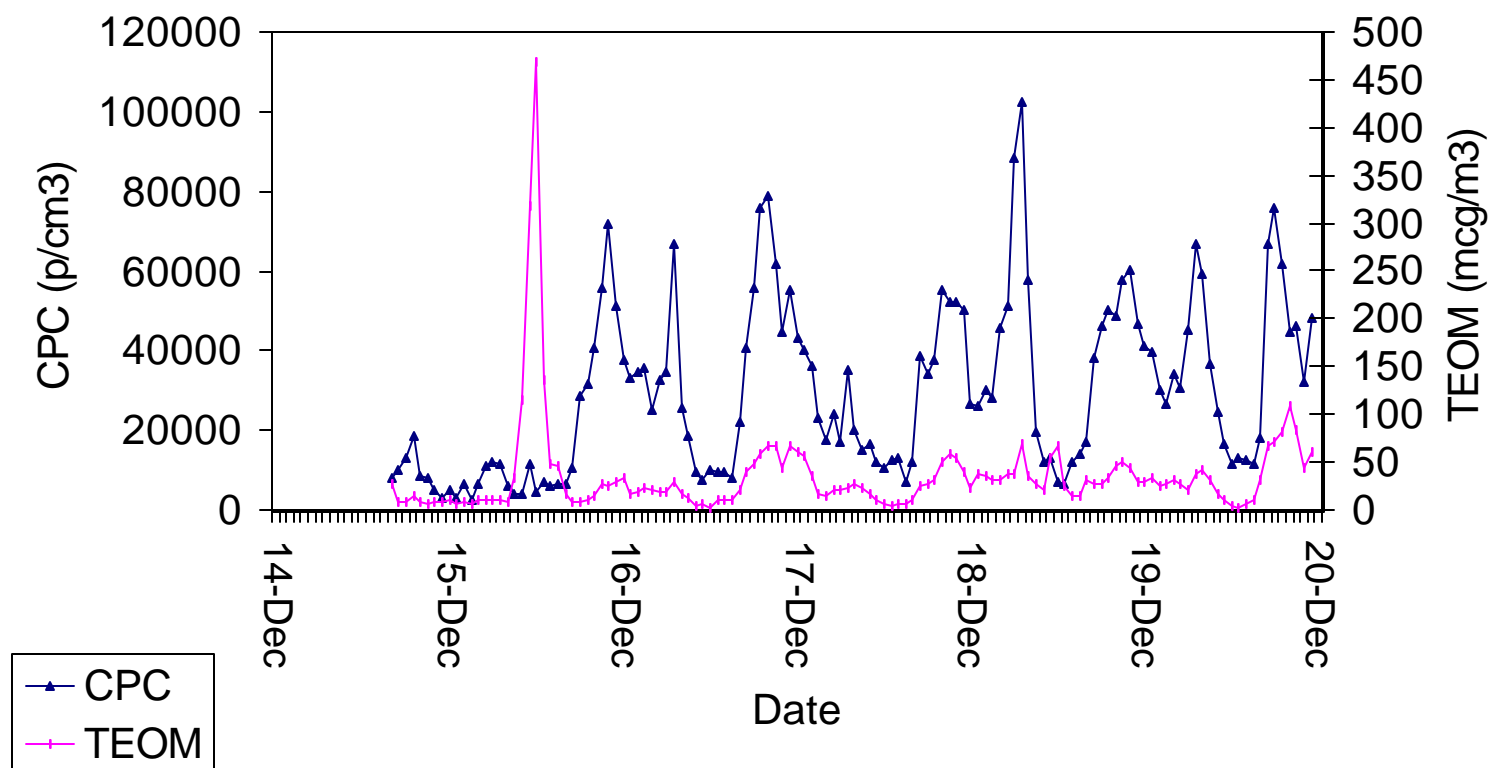
Total concentration of ambient particles at Rancho Los Amigos on 1/18/2001



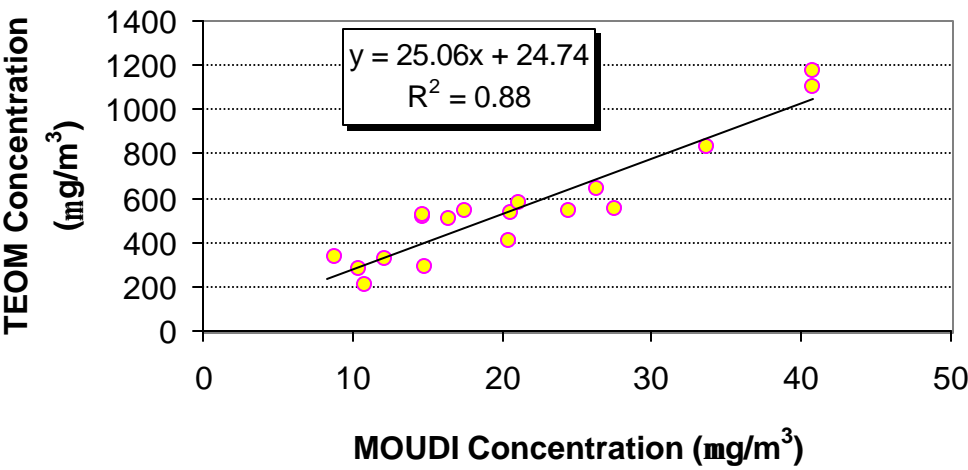
Total concentration of ambient particles at Rancho Los Amigos on 1/21/2001



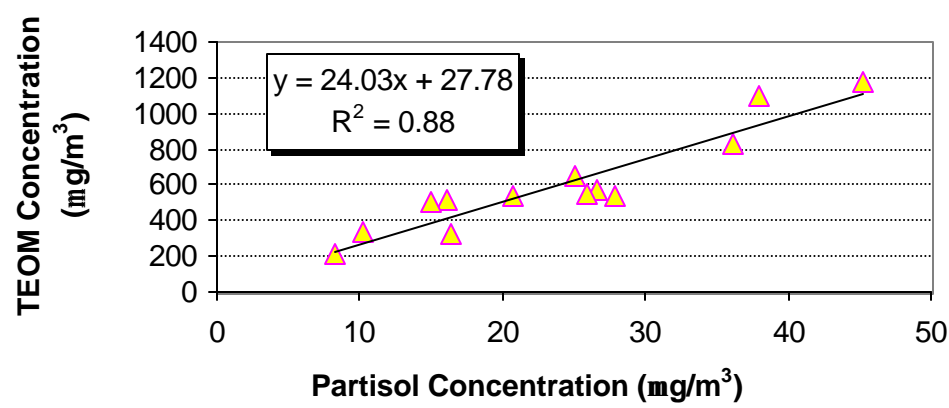
Lancaster CPC Data



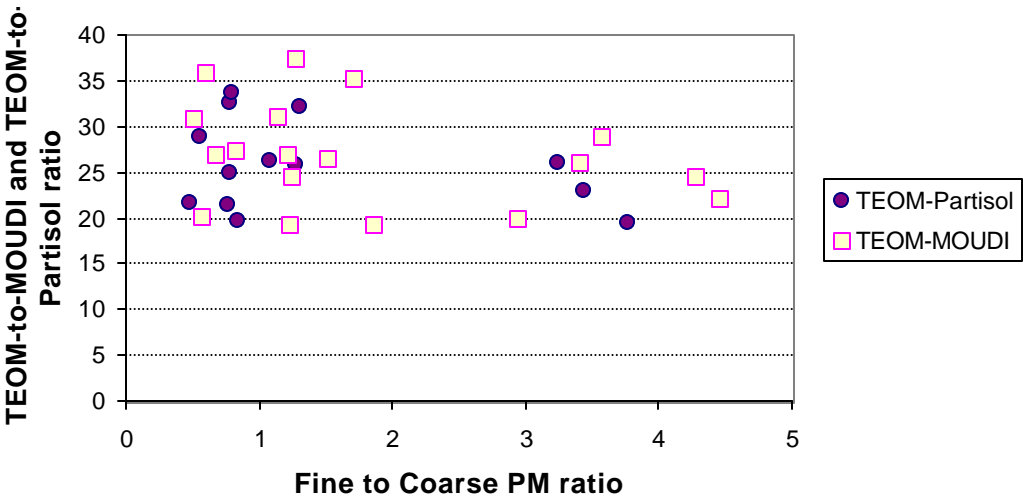
TEOM vs MOUDI Coarse PM Concentrations. TEOM at 50 deg C



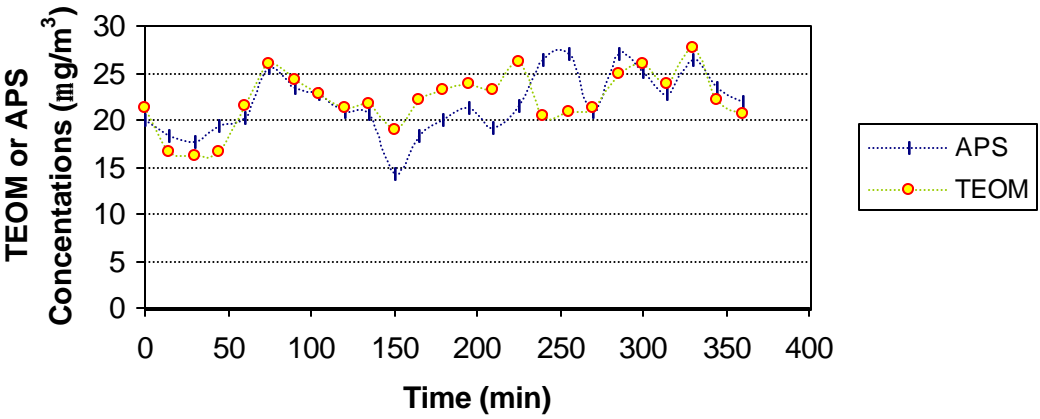
TEOM vs Partisol Coarse PM Concentrations. TEOM at 50 deg C



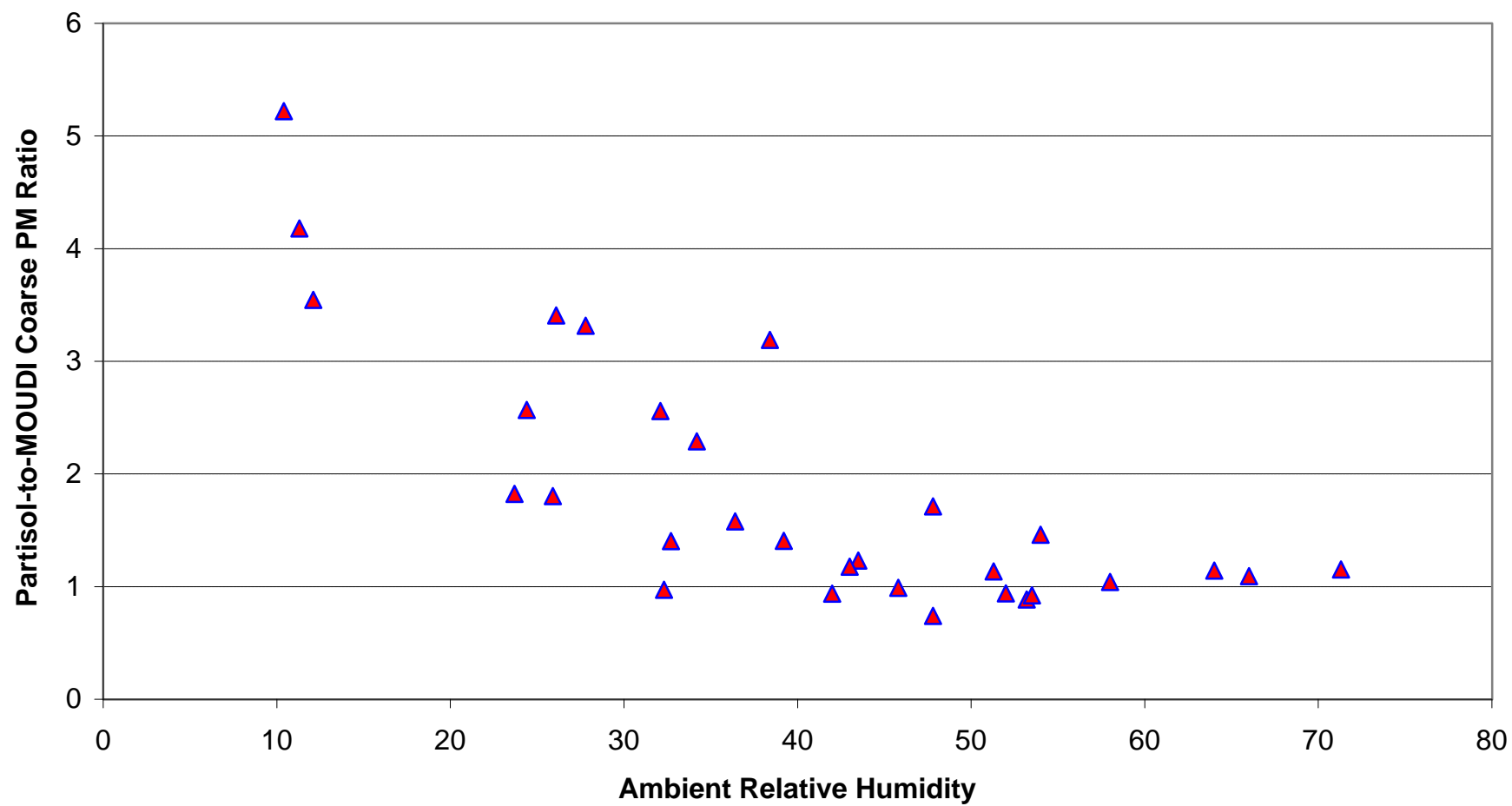
TEOM-MOUDI and TEOM-Partisol Concentration Ratio as a Function of Fine/Coarse PM ratio. TEOM at 50 deg C



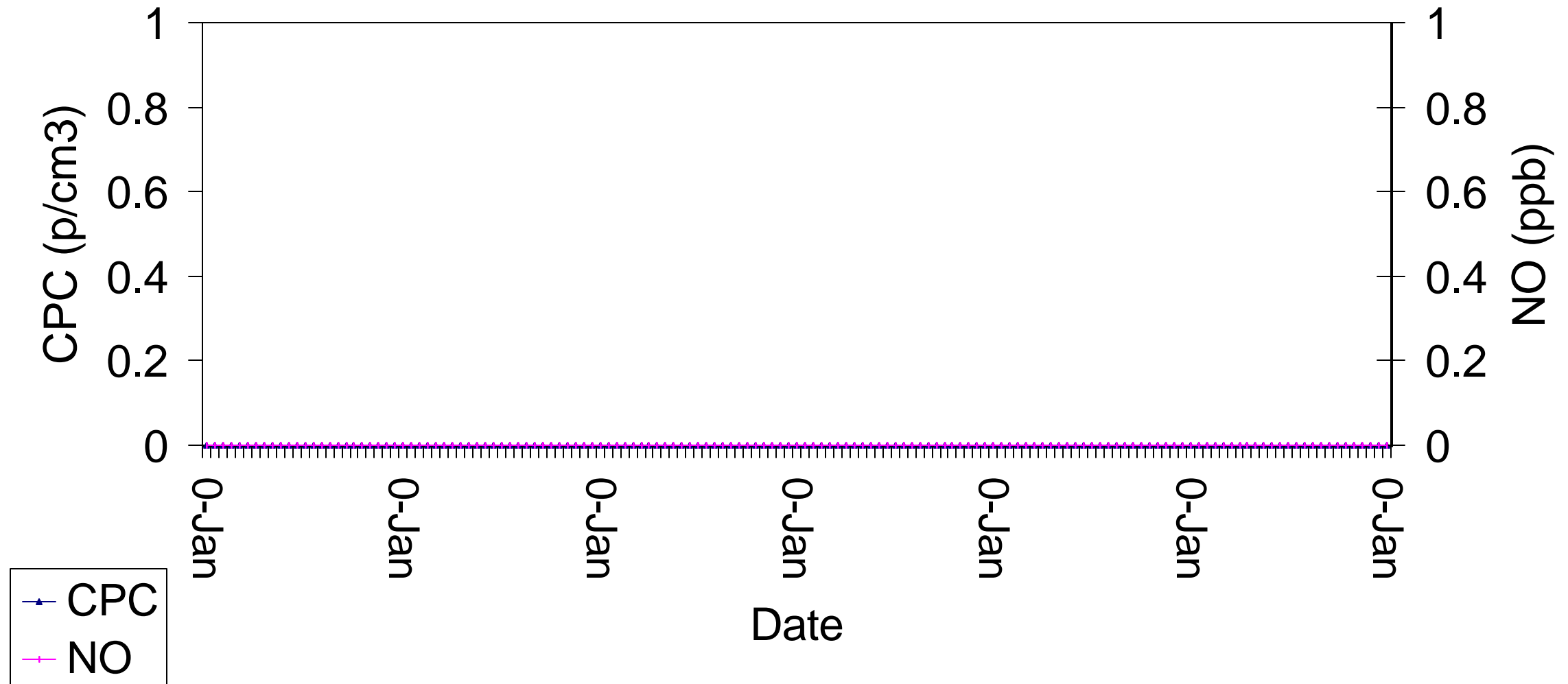
Time-series of TEOM and APS Coarse Particle Concentrations



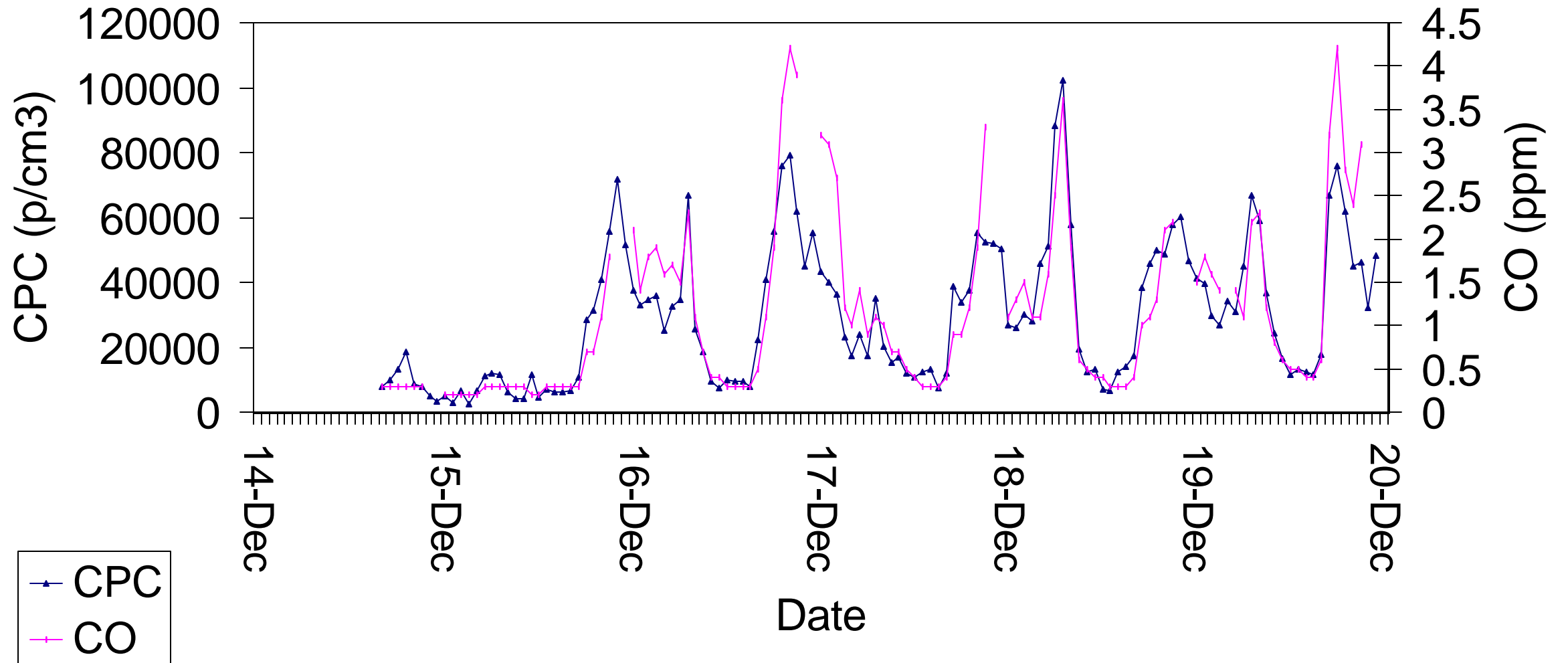
Plot of the Partisol-to-MOUDI Coarse Particle Concentrations as a Function of Ambient Relative Humidity



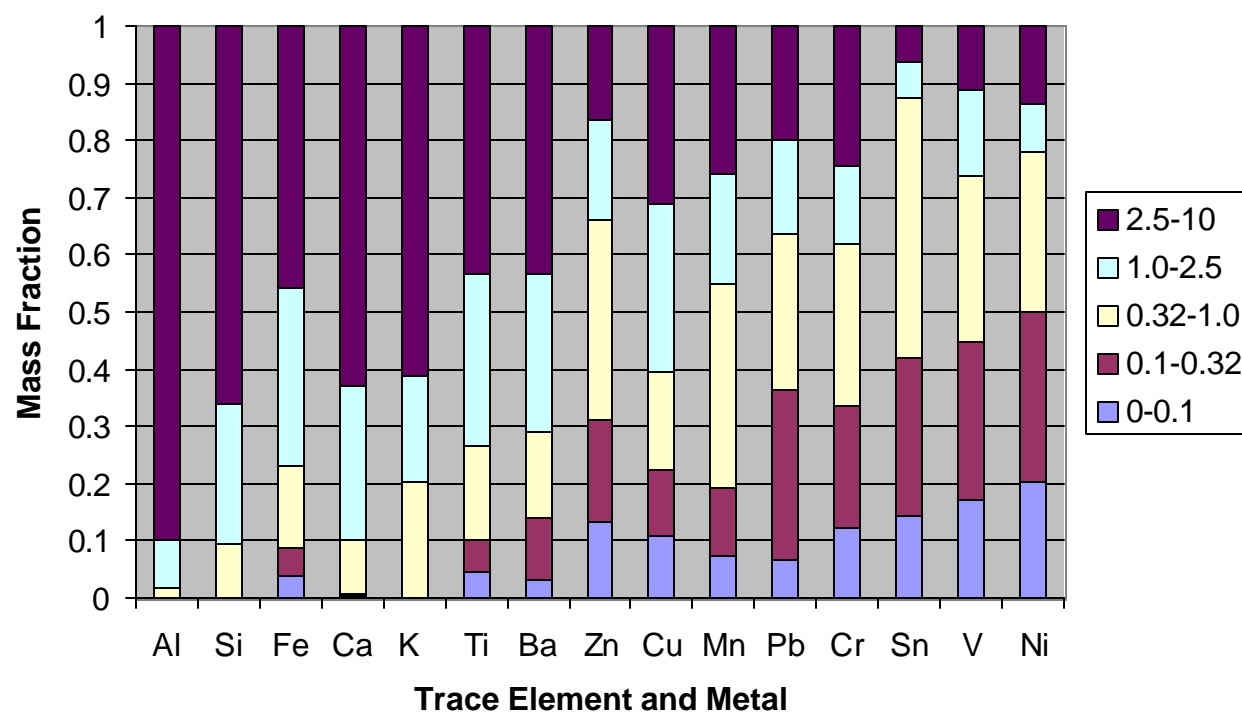
Lancaster CPC Data



Lancaster CPC Data



**Average Mass Fraction of Trace elements and Metals
in 5 particle size ranges. Based on nine 24-hr
averaged tests from October 3- December 29, 2000.
Location; Rancho Los Amigos**



Plot of the Ratio of Partisol-to-MOUDI Fine PM Concentrations as a Function of Relative Humidity

